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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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A REVIEW OF RECENT DEVELOPMENTS

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● APRIL 1962
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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., I. G. Dillon, P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Status of Fuel Recycle

The status of nuclear fuel processing and recycle is discussed by Culler[1] in the January 1962 issue of *Nucleonics*, Vol. 20, No. 1. The present stage in the development of processing methods for various types of fuel, assuming that aqueous solvent extraction is used as the separations technique, is shown in Table I-1.* No power-reactor fuel elements other than those for small fully enriched reactors have yet been processed. Work that will demonstrate and compare the various possible processes has started; this work is being done using highly irradiated fuel pins in full-activity small-scale laboratory experiments. The selection of the most desirable processes probably will require some pilot-plant experience.

Table I-1 WHERE WE STAND IN FUEL RECYCLE[1]

	Cold lab data	Cold engineering	Hot pilot-plant scale
Stainless-steel cladding (two feed-preparation processes possible):			
S.S.-UO_2 cermet	X	X	
UO_2 or ThO_2-UO_2 core	X	X	
Zircaloy cladding (two or three feed processes possible):			
Zirconium-uranium alloy	X	X	*
Zirconium-UO_2	X	X	
Zirconium-uranium-molybdenum	X	Partial	
Graphite-UC	X		
UC	X		
BeO-UO_2	X		
Aluminum- or magnesium-clad fuels	X	X	X
Niobium or NbC fuel	X		
Fluoride-base fused salts	X	Partial	

*Process used may or may not be used in the future.

Culler[1] states that the fluoride-volatility process that is now being developed is a strong competitor, as a separation method, for the solvent-extraction processes. There is confidence that fully enriched-uranium Zircaloy-clad fuels can be processed by this method. Fuels that contain plutonium can probably be processed; whether they can or not will depend on the engineering development that must follow currently promising chemical leads. An excerpt from reference 1 follows:

> The problems associated with the recycle of irradiated uranium, plutonium, thorium and U^{233} have yet to be faced by the private nuclear industry. Parasitically produced radioactive isotopes of these elements are present in recycled fuel; fuel elements incorporating plutonium or U^{233} must be refabricated behind shielding. In the development of closed-cycle techniques, the AEC development program is becoming particularly effective. For the special case of breeder reactors, integrated hot-fuel recycle development work for the fast breeder has been in progress for years at Argonne, Los Alamos, Atomics International and in other countries. For thermal breeders using thorium, a start has been made at Oak Ridge; a proposal made by Allis-Chalmers to the Italian government for a closed-cycle pilot plant and reactor is receiving very serious consideration. The plutonium-recycle-reactor effort at Hanford is supplementing other work aimed at recycling plutonium produced in converter reactors to make reactor fuel elements. The greatest gap in the developing technology is that for the recycle of thorium-U^{233}-U^{235} fuels such as those used in the Consolidated Edison reactor and an increasing number of others. The thorium fuel cycle should be placed on a comparable development basis with uranium-plutonium systems. This now appears to be the intention of AEC.

*Table I-1 is reprinted here by permission from *Nucleonics*.[1]

Culler[1] further states that the processing methods that are least costly to the government for processing returned fuels in existing facilities may not be the most economical fuel-recycle methods. During this decade it appears that the responsibility for providing a sound technological base for fuel recycle and waste disposal will be shouldered by the government. As the number of nuclear power reactors increases, industry will enter the fields of fuel processing and recycle using this technology, but probably not before 1970.

Fuel-Cycle Costs

Since the processing of nuclear fuels represents an appreciable portion of the cost of the nuclear fuel cycle, consideration is occasionally given to the philosophy of "burnup and discard" without processing and recycle. This approach is possible only if the burnup is high enough that the fissionable-material content of the spent fuel is too low to warrant recovery. This in turn implies very high neutron economy in order to achieve high burnup at low fissionable content.

The burnup and discard philosophy has been adopted by the Canadians for the first CANDU reactor, which will be constructed at Douglas Point, Ontario. This 200-Mw(e) power reactor will be fueled with Zircaloy-clad natural uranium dioxide, moderated with low-temperature heavy water, and cooled with heavy water in pressure tubes. Fuel charging and discharging will be accomplished while the reactor is at full power. The use of continuous bidirectional refueling will permit fresh fuel elements to be added to adjacent fuel channels from opposite ends. High burnups on the order of 8000 to 10,000 Mwd/metric ton of natural uranium are expected.

This approach to economic nuclear power depends upon the achievement of low fuel costs by burning low-priced (in Canada) natural uranium to compensate for the high capital cost of the nuclear power plant; the increment of higher capital cost is penalized less in Canada because of the lower annual fixed charge on capital investment. By the time that the growing nuclear power industry drives the price of natural uranium up to a level that is uneconomic for the "throwaway" fuel cycle, the techniques for recycling plutonium ought to have reached a stage of development to permit the CANDU plants to continue economical operation using new types of fuel elements that contain plutonium recovered from the stocks of previously discarded spent fuel. Each metric ton of such discarded fuel should contain about 3 kg or more of fissionable plutonium.[2]

Van Winkle[2] used U. S. cost accounting bases to estimate the fuel-cycle costs for the burnup and discard cycle for CANDU type reactors. Fuel costs, exclusive of heavy-water inventory but including fuel-inventory charges, were estimated to lie in the range of 1.50 to 1.90 mills/kw-hr, based on current fabricated fuel prices of $80 to $90/kg of uranium dioxide. Should the price of fabricated fuel decrease to the range of $50 to $60 after 1965, the fuel costs would be 0.94 to 1.28 mills/kw-hr. Using an annual fixed charge of 12.7 per cent and an estimated annual loss rate of heavy water of 2 per cent, the deuterium oxide cost is estimated at 1.02 to 1.20 mills/kw-hr.

The above fuel costs do not reflect the change in uranium prices put into effect[3] by the AEC on July 1, 1961. Herron[4] estimates that the new uranium price scale and the new 4.75 per cent per annum use charge will have the following effects on nuclear power costs.

	Total reduction in power cost, mills/kw-hr
Slightly enriched fuel, stainless-steel cladding	0.49
Slightly enriched fuel, Zircaloy cladding	0.46
Natural-uranium fuel throwaway cycle	0.22

The natural-uranium fuel cost is therefore reduced by only about one-half as much as the enriched fuels; however, the plutonium credit may also be affected by the new price scale. The AEC has implied that, after June 30, 1963, the plutonium credit may be based on its fuel value and has estimated that the fuel value of plutonium (formerly $12/g) would be reduced about 20 per cent by the revised charges for enriched uranium. Plutonium credit for slightly enriched reactors is in the neighborhood of 0.75 to 1.0 mill/kw-hr; hence a 20 per cent reduction would mean an increase in fuel-cycle cost

of roughly 0.15 to 0.20 mill/kw-hr. This increase does not occur in the throwaway cycle of the natural-uranium reactor.

A comparison of fuel-cycle costs for several reactors, including the natural-uranium heavy-water reactor and the slightly enriched-uranium pressurized-water reactor, has been published by Benedict et al.[5] Their estimates for the CANDU type reactor are, however, based on Canadian prices for uranium and are therefore not comparable with U. S. costs.

An article by Lane[6] on U. S. fuel costs for slightly enriched-uranium reactors discusses the following major technical advances that have led to the present encouraging outlook for competitive nuclear power: (1) perfection of vibratory-compaction and roll-swaging techniques to reduce fuel-element-fabrication costs, (2) achievement of large power densities, and (3) the capability of uranium dioxide and uranium carbide fuels to go to average burnups as great as 25,000 Mwd/metric ton. Lane stated that: "The combination of these advances leads to fuel costs in the range of 1.8 to 2.2 mills/kw-hr; it should be noted, however, that these low costs depend on continuation of existing AEC policies regarding lease of enriched uranium, reprocessing of spent fuel, and buyback of plutonium." Lane's statement probably refers to fuel costs for the near future rather than current costs.

An additional factor that must be considered in the comparison of the throwaway fuel cycle with the recycle philosophy is the high capital cost of the heavy-water reactor. This results from the large numbers of expensive pressure tubes and the special construction features needed to minimize deuterium oxide leakage loss. According to the cost accounting used by the Canadians, the fixed charges on this capital investment are not prohibitive, but in the United States these costs are high enough to account, to a large extent, for the lack of interest in this type of reactor and the throwaway fuel cycle.

Fuel-Processing Plans

For some time Italy's National Commission for Nuclear Energy (CNEN), with assistance from Vitro Corporation of America, has been exploring the possibility of building a chemical processing plant in Italy which will be capable of handling fuel enriched up to 90 per cent. The CNEN has discussed with Euratom the possibility of financial assistance for construction of the plant in the near future.[7] Although the processing plant will be primarily intended to meet the requirements of Italy's own research reactors, it will be flexibly designed to process up to 2500 fuel elements per year, or more than five times the expected initial throughput. The plant will be located near the CNEN's pilot uranium-thorium processing plant that is now under construction in the Lucania (Basilicata) region of southern Italy. Final design is to be completed and construction is to begin before the end of 1962. The plant is scheduled to be ready for testing by mid-1964. Tentative cost estimates for the completed plant are in the $3 million to $4 million range.[8]

The Eurochemic Company, which is constructing a chemical processing plant near Mol, Belgium, is also interested in obtaining Euratom's financial help. Cost estimates for the Eurochemic plant have risen about $9.2 million above the $12 million originally estimated. A plan to modify the Eurochemic plant to permit processing of material enriched beyond 5 per cent has reportedly been opposed by Italy's CNEN representative on the Eurochemic board.[7]

The General Electric Company has announced that it has discussed with the AEC a proposal to form a private company to undertake chemical processing of power-reactor fuels in leased facilities that are not now in use at the AEC's Hanford plant. Membership in the proposed joint company would be open to reactor manufacturers and to chemical companies but not to reactor owner-operators. The joint company would operate only for a definite transition period until the processing load is sufficient to support a competing plant. Any participant who wished to establish a competing company could elect to withdraw at any time. The plan is in an early stage, and the AEC has not yet indicated interest in pursuing the proposal.[8]

Commissioner Wilson,[9] in a recent statement on USAEC policies relative to foreign reactors, remarked that:

> ... the AEC expects to retire from the processing business on commercial fuel elements if such service becomes available on a reasonable basis from private concerns. We have real hopes that this will take place within the next few years, both in the United States and in Europe at least, thus avoiding the considerable costs and incidental hazards of

long-distance shipping of spent fuel. The same will probably be true in Japan within a reasonable period. In order to assist in the establishment of chemical processing services outside of the AEC, we are prepared to aid those contemplating the construction of such facilities for power reactor fuel elements through the providing of technical assistance.

The AEC is committed to pay compensation for all domestically produced plutonium and U^{233} returned to the Commission, according to guaranteed prices[10] in effect through June 30, 1963. Beginning on July 1, 1962, the buy-back price for plutonium will be $30/g. Wilson observed that "it may be necessary for our government to establish guaranteed prices for plutonium and U^{233} produced in domestic reactors for several years beyond 1963. Our current thinking is that the price would be based on an estimated fuel value." The fuel value of plutonium and U^{233} was discussed in the October 1961 issue of *Reactor Fuel Processing*, Vol. 4, No. 4. Wilson[9] also commented that, although not conclusive, recent results of studies in connection with the Plutonium Recycle Test Reactor lead to optimism regarding the comparative value of plutonium as a reactor fuel, at least in certain types of reactors.

Fuel-Processing Literature

An 86-page bibliographic USAEC report entitled Reprocessing of Irradiated Fission Reactor Fuel and Breeding Material, TID-3529 (2nd Rev.), is available from the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. The publication lists 893 unclassified references and their availability, including 166 technical papers and reports originating outside the United States.

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8. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 9(1): (January 1962).
9. Remarks by Robert E. Wilson, Commissioner, U. S. Atomic Energy Commission, Prepared for Delivery at Second Joint Conference on Nuclear Power, U. S.–Japan Atomic Industrial Forums, Tokyo, Japan, December 5, 1961, AEC Press Release 5-27-61.
10. *Federal Register*, Notice 25 FR 12255 (Nov. 30, 1960).

Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

All means presently utilized (other than experimentally) to recover uranium and plutonium from fuels discharged from nuclear reactors involve dissolving in aqueous reagents followed by primary separation of the desired materials with organic solvent extractants. Precipitation, ion exchange, and other techniques are utilized to supplement the primary processes. Most fuels from the newer power and special-purpose reactors now being installed will, in all likelihood, be processed by similar techniques for many years. Consequently extensive process-improvement studies are warranted for present processes, whereas the increasing complexity of reactor fuels requires the development of new and modified aqueous processes for efficient fuel recovery.

Preparation for Fuel Processing

The principal means of preparing spent nuclear fuel assemblies for separation processing include the mechanical removal of cladding material and other non-fuel-bearing portions, mechanical disintegration, and separate or integral chemical dissolution of the sheath and fuel portions.

Mechanical Processing Methods

Du Pont[1] reports on an underwater, remotely operated and maintained tube cutter. The cutter, which will accommodate up to $4\frac{1}{4}$-in.-diameter tubing, has operated satisfactorily while cutting uranium metal and uranium-zirconium alloy of $\frac{1}{4}$-in. wall thickness and aluminum-uranium alloy of $\frac{3}{16}$-in. wall thickness. Some very small particles were produced, but contamination was controlled.

The tube cutter shown in Fig. II-1 is similar to a pipe cutter except that the tube is rotated in the device; in a pipe cutter the frame and cutting wheels rotate around the tube. A hydraulic ram forces the wheels of the tube cutter into the tube. A mechanical backstop prevents the ram from retracting as the wheels pass over uneven or hard spots in the tube. The frame is mounted at an angle to permit visual observation of the cutting wheels. One side of the two-piece frame can be swung open to facilitate the remote replacement of wheels and the insertion and removal of tubes. Sufficient adjustment is provided to accommodate tubes up to $4\frac{1}{4}$ in. in diameter and $\frac{3}{8}$ in. in wall thickness.

To minimize the spread of radioactive particles and dissolved material released during the cutting operation, an enclosure around the cutter directs a flow of water down over the cutting wheels and directly to a decontamination facility. A removable screen at the outlet of the enclosure catches large pieces that might be produced by the fragmentation of brittle tubes.

Nineteen cuts were made through fuel tubes of uranium metal and uranium-zirconium alloy that had been irradiated to 1500 to 2500 Mwd/metric ton. A force of 3000 lb was required, and the cutting time was 5 min per cut. Thirty-five cuts were made through tubes of alumipum-uranium alloy with a 3-in. diameter and a $\frac{3}{16}$-in. wall thickness.

Hanford Atomic Products Operation (HAPO) has issued a final report[2] on the development of a shear for fuel-element cutting. This work is described in previous Reviews,[3,4] but the final report[2] gives some conclusions on blade life and mechanical features. The two best moving blades were a male Vee blade made of silicon-manganese tool steel (S type) and a straight steel blade edged with cobalt alloy (Stellite 6).

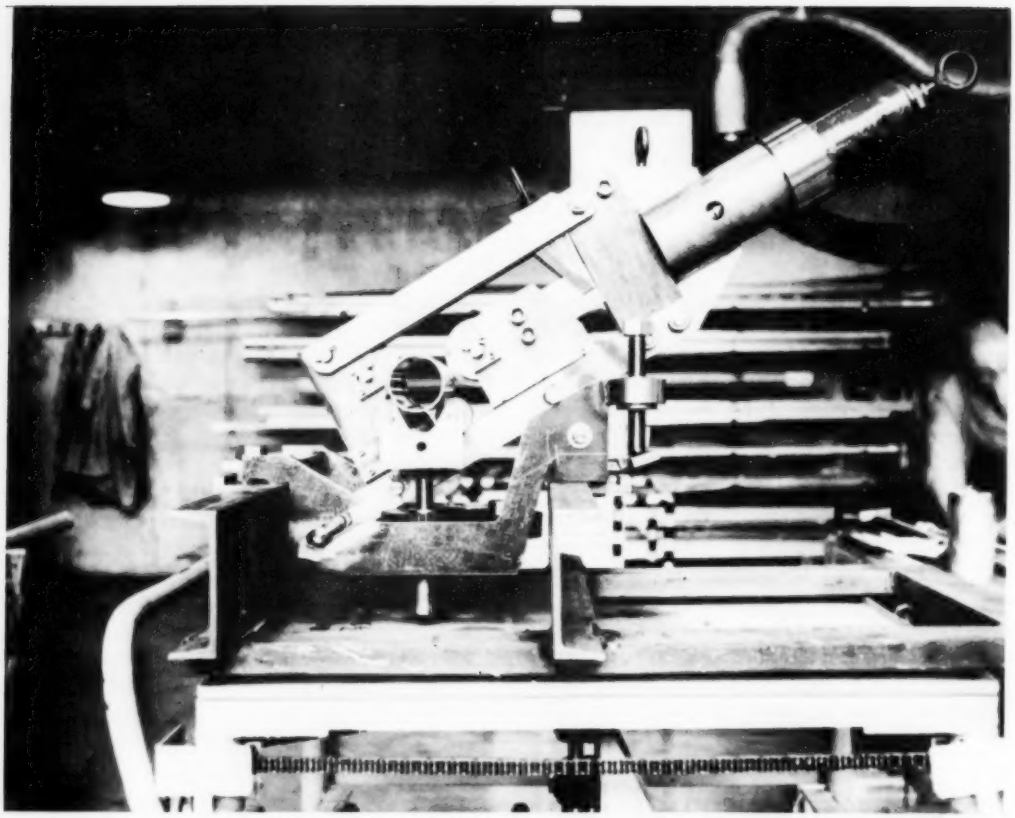

Fig. II-1 Hydraulically actuated tube cutters.[1]

The Vee blade cuts with less shock and, initially, cuts with less applied force than the straight blade. However, the Vee blade is also less durable; therefore the cutting effectiveness of the two blades is about equal. It is concluded that a production shear should be capable of using either, the ultimate choice being based on extended experience.

Three main conclusions were drawn from the studies at HAPO:

1. Water-submerged shearing, conceived for the Hanford process to control dust, fires, and fuel temperature, also offers three mechanical advantages: (*a*) the water lubricates the shear and transfer mechanisms, (*b*) mechanisms stay cleaner so that fewer jams and malfunctions occur, and (*c*) the presence of a water level in the shear feed trough is an infallible indication that the dissolver basket is properly positioned beneath the shear.

2. The shear must be designed so that corrective action may be readily undertaken when the inevitable jams occur.

3. Feasible techniques for shear maintenance can be developed for in-cell replacement of individual shear parts (e.g., blades), components, or the complete assembly. The component-replacement approach is recommended to minimize handling of the massive shear frame since the stationary blade will be replaced less often than the moving blade.

In general, the report[2] is a good over-all primary source for the data and results of the work done by HAPO on shearing of fuel elements. A correlation is also included which uses a shear factor K defined by the simple shearing equation:

$$F = KAS \qquad (1)$$

where F = shear force
A = cross-section area of cut material
S = shear strength of the material

For the hydraulic shear, factor K was further defined by

$$K = \frac{PA_p}{AS} = \frac{PA_p}{A_1S_1 + A_2S_2 + \ldots A_nS_n} \quad (2)$$

where P = initial system hydraulic pressure, i.e., system pressure prior to start of the shearing stroke
A_p = shear piston area
A_n, S_n = area of cross section and shear strength, respectively, of the nth component of a composite work material

According to Eq. 2, factor K is not computed from an actual shear force but from a shear system "input." Thus K is not a fundamental property of the cut material and only gains significance through comparison.

Shear strength S, like K, also requires a note of explanation. Since a means of measuring true shear strength is not available for all materials, the definitions given by Vose are used in the report[2] for calculating K: For ductile materials,

$$S = 0.6 \times \text{ultimate tensile strength} \quad (3)$$

and, for brittle materials,

$$S = 0.1 \times \text{ultimate compressive strength} \quad (4)$$

Although the values for S as given by Eqs. 3 and 4 are only approximate, they are consistent with the range of results obtained in actual shearing operations.

Oak Ridge National Laboratory[5,6] reports on the use of their inclined-drum rotary leacher as a conveyor from a chopper.[7] Color-coded stainless-steel rods (1/2 in. in outside diameter × 1 in. long) were fed to the leacher to evaluate backmixing. About 40 per cent of each charge "backmixed," and some pieces migrated as far back as 4 to 5 flights. It was found that the backmixing was a result of open gaps between flights. Modifications will be made to correct this.

Total Dissolution of Fuel Material

Dissolution of Uranium and Uranium Alloys. In conjunction with an earlier plan for the processing of certain power-reactor fuel materials at Hanford, studies of dissolving uranium-molybdenum alloys in nitric acid were undertaken. Blaine[8] has reported on pilot-plant studies using a trough dissolver with airlift recirculation of dissolving reagent from a reservoir. From comparison studies with cast unalloyed uranium, it was concluded that dissolution rates in the recirculating device were essentially the same as in a batch system. Dissolving of an alloy of uranium containing 3 per cent molybdenum is complicated by precipitation of molybdenum at low (less than about 4M) and high (over 11M) acidity. The low-acid precipitate, which can be eliminated by adding ferric nitrate, carries much uranium, whereas the high-acid precipitate does not.

The dissolution of uranium-molybdenum alloy is considerably faster than that of uranium at comparable acidity. For example, uranium–3 per cent molybdenum dissolved at 15 to 45 mils/hr in 4M nitric acid as compared to 1 to 2 mils/hr for unalloyed uranium. The presence of up to 1.0M ferric nitrate accelerates dissolution somewhat, whereas uranyl ion suppresses it. If molybdenum-uranium precipitated during dissolution, it could be redissolved by increasing the acidity.

If irradiated uranium is dissolved prior to the decay of eight-day I^{131}, the latter may be substantially evolved in the off-gas. Cederberg and MacQueen,[9] in studies of iodine control in recovering Ba^{140} from short-cooled Materials Testing Reactor fuel elements, reported that iodine may be removed efficiently from process off-gases by 1.0M sodium hydroxide that contains 0.1M sodium thiosulfate, by 5 per cent nitric acid that contains 0.001M mercurous and mercuric nitrates, and by beds of activated charcoal.

Dissolution of Zirconium-Rich Fuels. Alloys of zirconium or Zircaloys which contain 1 to 10 per cent uranium (clad in a Zircaloy) constitute an important class of highly enriched uranium fuel materials. The chemically resistant nature of zirconium requires the use of fluoride systems (hydrofluoric acid, or ammonium fluoride with minor amounts of oxidants) to dissolve such fuels.

Studies are being made at the Idaho Chemical Processing Plant to adapt the hydrofluoric acid dissolution process to continuous operation. A Zircaloy-2 dissolving rate of 37 mg/(cm^2)(min) was noted in a hot 10*M* fluoride solution that contained 1.0*M* zirconium.[10] Product concentrations of as much as 2.2*M* zirconium have been obtained.[11]

Other modifications of the hydrofluoric acid process are aimed at precipitating zirconium and fluoride from the dissolver solution to increase process-system capacity and to reduce waste volumes and corrosiveness. Precipitation of barium fluozirconate with solid barium nitrate at room temperature (investigated for corrosion reasons) was found to be much slower and less efficient than at 95°C; with dissolved precipitants the reagent volumes that were required were excessive.[12] In another procedure, more than 97 per cent of the zirconium was removed by treating hydrofluoric acid dissolver solution with sodium formate at 60°C or higher. The addition of flocculating agents aided precipitate separation.

Gens and Blanco[13] have recently reviewed the status of the ammonium fluoride–ammonium nitrate–peroxide process for dissolving zirconium alloys that contain up to 10 per cent uranium. The flow sheet was previously presented.[3] Batch dissolutions of alloys that contained as much as 8 per cent uranium were conducted on a pilot-plant scale;[5,6] the reagents that were used contained about 6.5*M* ammonium fluoride and up to 0.6*M* ammonium nitrate, with peroxide being added continuously so as to maintain its concentration at about 0.01*M*. Since 30 to 70 per cent hydrogen was found in the off-gas following the condenser, dissolutions were attempted in the absence of ammonium nitrate. The dissolving process proceeded as well in the absence as in the presence of this reagent. More recently, successful studies have been made of the continuous dissolution of simulated zirconium fuel using the ammonium fluoride–nitrate–peroxide reagent.[14]

In further studies of reagents that are compatible with titanium vessels and are capable of dissolving zirconium and its alloys, Clark and Gens[15] studied the use of chromate in concentrated nitric acid that contained a small amount of hydrofluoric acid. There is considerable similarity in the behavior of zirconium and titanium under chemical attack. Titanium is more resistant in oxidizing solutions, and zirconium is more resistant under reducing conditions and is more readily attacked by fluorides. A preliminary flow sheet for the dissolution of a 6.3 per cent uranium alloy is given in Fig. II-2; this process uses 16*M* nitric acid that contains 1.9*M* hydrofluoric acid and 0.58*M* chromate. Dissolving rates of 2 mg/(cm^2)(hr) are predicted, and titanium corrosion should not be severe.

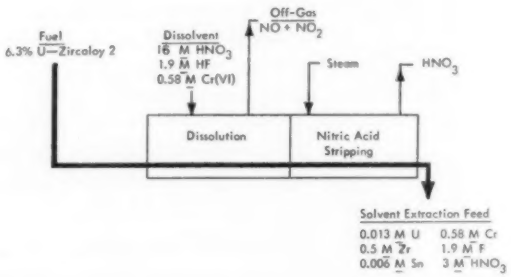

Fig. II-2 Process for dissolving zirconium alloy reactor fuels in titanium equipment.[15]

Dissolution of Chromium, Nickel, and Iron Alloy Fuels. The fuel that was utilized by General Electric Company's Aircraft Nuclear Propulsion Dept. in a series of Heat-Transfer Reactor Experiments (HTRE 1, 2, and 3) is composed of an assembly of concentric cylinders. Each cylinder consists of a 5-in.-wide thin band of Nichrome-V alloy (80 per cent nickel and 20 per cent chromium), modified by the addition of 1 per cent niobium; the core of the band contains a sintered matrix of mixed uranium dioxide–Nichrome powders. The outer cylinder is 3.43 in. in diameter. A series of the concentric bands is assembled on stainless-steel rails. The over-all composition of a typical assembly was calculated as follows:

	Wt.%
Uranium dioxide	23.7
Nickel	58.7
Chromium	15.1
Iron	2.1
Niobium	0.4

Many of the assemblies also have ceramic-insulated noble-metal thermocouples firmly attached to them.

Extensive work to develop means of processing these fuel elements has been carried out at the Idaho Chemical Processing Plant. The laboratory work was recently summarized by Cannon et al.[16]

Nichrome is quite resistant to chemical attack, its resistance being attributed to its chromium content. Both the separate dissolution of Nichrome and uranium dioxide and the integral dissolution of these components were considered in developing a process for the HTRE fuel. Nichrome can be attacked more rapidly than the uranium dioxide by concentrated halogen acids and by mixtures of halogen acids with concentrated phosphoric or sulfuric acid, but, in all reagents examined, the indicated loss of uranium to the Nichrome solution was too large to be tolerated.

Only two reagents that are capable of dissolving uranium dioxide (concentrated perchloric acid and mixtures of nitric and hydrochloric acid) have been found to effect the complete dissolution of Nichrome at reasonable rates. Nichrome may also be electrolytically dissolved in nitric acid. Dissolution in dilute nitric-hydrochloric acid mixtures, which seemed most practical for plant application, was used in further work. The process is accordingly similar to the dilute nitric-hydrochloric acid dissolving method used for stainless-steel fuels (known as the Darex process). Titanium appears suitable for the construction of process vessels. After the chloride is removed, a nitric acid extraction feed solution is produced which is similar to that used in applications of the Purex process.

When Nichrome is dissolved under boiling conditions, rates acceptable for process operation can be obtained over a wide region of reagent compositions (as shown in Fig. II-3), although maximum rates are produced by a mixture of 4*M* hydrochloric acid and 6*M* nitric acid [43 mg/(cm^2)(min)]. The rate of dissolution is affected little by metal-salt concentration, and dissolver products containing 50 to 100 g of metal salts per liter can readily be obtained. The stainless-steel supporting ribs of the HTRE fuel are also readily dissolved, but niobium in the cladding material and silicon from the brazing alloy form insoluble hydrated oxides. Small amounts of (1) refractory oxides of chromium and nickel which are formed on the fuel cladding and (2) thermocouple metals and insulators may also appear in the insoluble

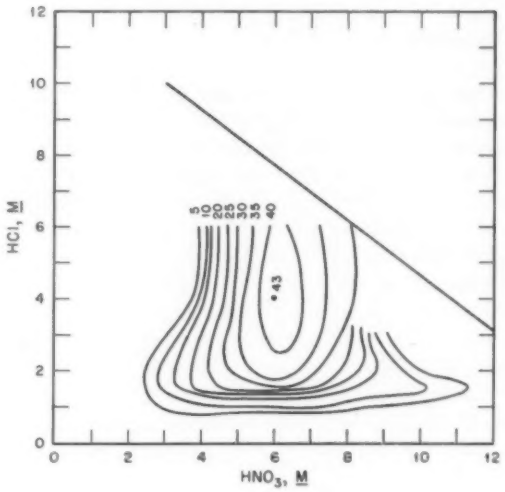

Fig. II-3 Initial dissolution rates of Nichrome-V containing 1 per cent niobium in boiling nitric-hydrochloric acid mixtures.[16] (The rates are given in milligrams per square centimeter per minute.)

residue. Off-gases are chiefly nitrogen oxides, chlorine, and nitrosyl chloride.

Studies on the characteristics of the solids that remained after dissolution indicated that they could be readily removed by either filtration or centrifugation. The solids can be washed free of uranium with 0.1*M* nitric acid. Alternatively the bulk of the solid residue (except for chromium oxide and alumina) can be placed in solution with dilute hydrofluoric acid. Chloride can be removed from the dissolver-product solution to a level that will permit solvent extraction (by distillation) in stainless-steel equipment (as in the Darex process).[17] Removal by stripping facilitates reuse of hydrochloric acid in the dissolving reagent. It is also noted in reference 12 that some volatilization of ruthenium was observed in the chloride-removal process and that chloride may be removed, or its corrosive effects may be minimized, by oxidation, precipitation, or complexing.

The solution that results from either batch or continuous chloride removal is highly acidic (of the order of 10*M*). Tributyl phosphate (TBP) process-extraction flow sheets were developed for feed solutions that ranged from 5*N* to 8*N* in acidity (produced by dilution), with 15 to 30 per cent TBP in diluent. The highly acidic organic phase may be contacted with a basic aluminum

nitrate scrub to reduce its acidity and to permit stripping.

Because of the interest in developing a process for dissolving stainless-steel fuels in dilute aqua regia mixtures and the lack of understanding of the mechanism for this reaction, Cannon[18] attempted to develop empirical rate expressions for the dissolution of pure iron and nickel in various nitric-hydrochloric acid mixtures at 50 to 80°C. No general relations were found which included the concentrations of both acids. The following relation for iron was found between the rate constant R [change in concentration with time (in minutes)] and the hydrochloric acid concentration in the range 0 to $3M$ for $2M$ nitric acid solutions and a temperature of 50°C.

$$R = 1{:}34 \times 10^{-4}\,(\mathrm{HCl})^{-0.62}$$

Studies with iron were also made in $2M$ hydrochloric acid with nitric acid concentrations that ranged from $1M$ to $4M$, but neither marked nor consistent effects on dissolution rate were observed. Studies with nickel were conducted at 80°C and at higher nitric acid concentrations. For constant ($7M$) nitric acid concentration and hydrochloric acid concentrations ranging from 0 to $2.5M$, the rate constant was found to depend on hydrochloric acid concentration as follows:

$$R = 4.67 \times 10^{-5}\,(\mathrm{HCl})^{1.38}$$

For nickel in solutions of constant ($1.5M$) hydrochloric acid concentration and nitric acid levels ranging from $5M$ to $7M$, the rate constants corresponded to

$$R = 1.76 \times 10^{-8}\,(\mathrm{HNO_3})^{4.18}$$

The wide variations in the values of the exponents and the difficulty in expressing the nitric acid dependence in dissolving iron indicate that these data cannot be used in developing a simple mechanism.

Electrolytic dissolution of stainless steel, used either as cladding or matrix material for nuclear fuels, is of considerable interest since it is thereby possible to dissolve in nitric acid alone; therefore the severe corrosion problems that accompany the use of dilute aqua regia or sulfuric acid–nitric acid exposure are avoided. Bomar[19] has recently described a series-electrolytic dissolver concept in which there is no problem of making contact between fuel and electrodes. The principle is illustrated in Fig. II-4. The dissolver consists of a simple tube having electrodes at each end. The electrodes need not make physical contact with the dissolving metal; they merely serve to introduce current that then passes into solution. The containing vessel is either a nonconductor of electricity or it may have an insulating lining to avoid bypassing of current. Fuel pieces are randomly located in the solution between the electrodes. The current flow effectively forms a series of electrolytic cells between adjacent fuel pieces, each of which dissolves at its anodic end.

Dissolving tests have been conducted in small glass- and titanium-lined vessels, using $8M$ nitric acid electrolyte, at 10 to 130 volts and 1 to 3 amp. As a result of the series-cell effect, the amount of metal dissolved was as much as 10 times that equivalent to the current passed. Product streams that contained over $2M$ solutions of the metal cations were readily obtained.

Treatment of Nonmetallic Fuels. The treatment of various uncoated and coated graphite fuel elements that carry uranium and thorium

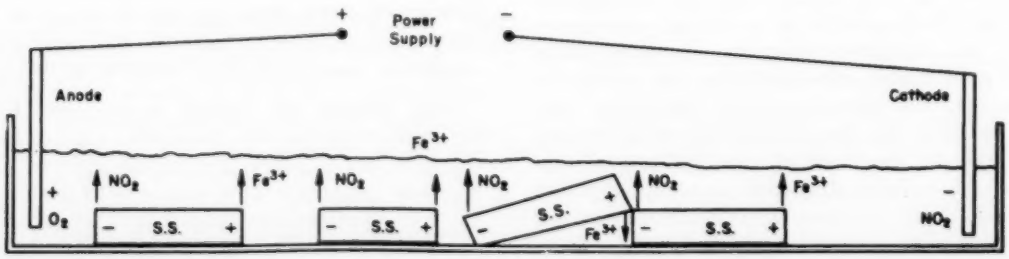

Fig. II-4 Principle of series electrolytic dissolver.[19]

has been studied extensively at Oak Ridge. It was recently reported[14] that treatment of silicon carbide-coated prototype Pebble-Bed Reactor spheres that contained graphite impregnated with thoria, by reacting with 90 per cent nitric acid, resulted in about a 6 per cent uranium loss to the residue. After treating for 4 hr, the fuel was mostly disintegrated to particles smaller than 4 mesh. More uranium remained in particles finer than 100 mesh than in the coarser particles, although the silicon carbide coating was uniformly distributed.

Tarpley and Winchester[20] report that ultrasonic activation can be applied to markedly increase the rate of leaching of uranium dioxide from uncoated graphite fuel material, both from particles produced by grinding and from massive plates. Tests conducted on the pulverized material with 16- to 30-mesh particles, which originally contained 2 per cent uranium in boiling 16*M* nitric acid, yielded 91 per cent uranium recovery in two leaches without ultrasonic treatment and 96 per cent recovery when treated similarly with ultrasonic activation at a frequency of 20 kc and an energy input of 300 watts per 10 g of graphite. In other tests where the graphite contained 4 and 11 per cent uranium, high recovery was obtained both in the presence and absence of ultrasonic energy. More interesting results were obtained by the use of essentially intact $\frac{1}{4}$-in.-thick impregnated graphite plates. Under similar conditions of acid contact, 98 per cent of the uranium was leached in 10 hr from a plate that originally contained 2 per cent uranium with the ultrasonic transducer directly coupled to the plate, compared to only 72 per cent without ultrasonic activation. Twenty-hour treatments resulted in 99.8 and 92 per cent recoveries, with and without ultrasonic activation. This suggests that uranium might be recovered from certain graphite fuel-element shapes without disintegration.

Separations Processes

Feed solutions are generally prepared for separation by solvent extraction, but ion exchange, precipitation, or other separating techniques may also be utilized.

Solvent-Extraction Processes

Extraction-Process Studies. In continuing work on the processing of fuels utilized in the thorium-U^{233} cycle, Oak Ridge recently noted the results of a preliminary test with short-decayed irradiated thoria.[14] In a single cycle, all the thorium and uranium and 85 per cent of the protactinium were extracted from a nitrate solution, with TBP in hydrocarbon diluent, with a decontamination factor of 40,000 from rare earths, 1400 from ruthenium, and 100 from gross gamma activity. This indicated that it would be possible to process 90-day-cooled Consolidated Edison reactor fuel to recover 99.9 per cent of the fissionable and fertile material and to remove over 90 per cent of the important neutron-capturing fission products in a simple process. The separation of protactinium from a simulated product solution by adsorption on crushed unfired Vycor glass was also studied. About 60 per cent of the protactinium was removed from a 10*M* acid solution. Fired Vycor glass did not adsorb protactinium. In later work[21] improved adsorption was noted at slightly lower acidities. Elution was obtained with dilute oxalic acid.[22]

In the TBP extraction processes, difficulties that appear to be related to solvent deterioration are sometimes encountered in the decontamination of products from Zr^{95} and its daughter product Nb^{95}. Studies at Oak Ridge on the extraction of niobium by TBP were aimed to clarify this problem.[23] A multiple contact technique was used to determine the distribution coefficients in the extraction of pure niobium tracer from nitric acid solutions. Organic phase (30 per cent TBP) from the initial contact was recontacted with further volumes of nitric acid, whereas the aqueous phase was treated with additional volumes of organic phase at equilibrium acidity. Although the initial organic-to-aqueous niobium distribution coefficients were of the order of 0.01 (aqueous phase 2*N* in nitric acid), distribution coefficients into more organic phase decreased to the order of 0.003 to 0.006; whereas, in reextracting niobium into fresh aqueous phase, distribution coefficients as high as 1.1 were observed. This suggests that there are more than one species of niobium present and that the net effects of various mixtures are observed. It was further noted that if the solvent contained TBP that had been degraded by nitric acid refluxing, niobium distribution coefficients as high as 30 could be obtained.

Extensive data that were obtained by Russian workers for the extraction of tetravalent plu-

tonium by TBP have recently been reported in translated form.[24] Data are given over the range of aqueous-phase nitric acid concentrations of 0.5*M* to 10*M* and uranium concentrations of 0.02*M* to 1.26*M* for equilibration with 20 per cent TBP at 20 to 70°C. Another Russian article[25] reports some distribution data for uranium between 20 per cent TBP and 1*M* to 15*M* sulfuric acid. It was shown that TBP is a poor extracting agent for uranium from sulfuric acid since the distribution coefficients increased from 0.004 to only 2.2 as the acid strength increased. Behmoiras and others[26] studied the performance of pulse columns in uranium extraction with diluted TBP by measuring decontamination from minor quantities of thorium present in the feed solution. It was noted that, in a particular column, best separation and most efficient operation were obtained at about 85 per cent saturation of the organic phase rather than at full saturation as anticipated.

In the separation of plutonium from uranium by the Purex process, ferrous sulfamate is usually used to reduce the plutonium to a relatively inextractable state. Under suitable conditions the same result can be accomplished with tetravalent uranium ion. The use of tetravalent uranium ion, if derived from the uranium product stream in the process, avoids the addition of iron and sulfate salts to the process waste stream. The practicality of using tetravalent uranium depends on the development of simple preparation methods adapted to the process streams. Ondrejcin[27] recently described a method to make a nitrate solution in high yield by reducing hexavalent uranium in sulfuric acid with zinc and by precipitating hydrated uranium dioxide with sodium or ammonium hydroxide. The latter is dissolved in nitric acid that contains hydrazine as a holding reductant to prepare the plutonium-reducing reagent.

Preliminary work has been done at Oak Ridge on a process for final recovery and purification of plutonium separated in a Purex type process by amine extraction.[7] Coleman[28] has since described modifications of this process and a successful batch countercurrent test. Ferrous sulfamate-reduced plutonium in 1.5*M* nitric acid solution was extracted with $^1/_{12}$ volume of 0.3*M* trilaurylamine in diethylbenzene. The extract was scrubbed with dilute nitric acid, and plutonium was stripped with $^1/_{20}$ the original volume of 3*M* acetic acid. Flowing stream losses to both raffinate and stripped organic were quite low, although precise measurement was obscured by the presence of americium in the raffinate. To test decontamination, tracer zirconium was added to the feed. A zirconium decontamination factor of the order of 50,000 was reported for the final product.

Solvent Degradation and Treatment. The TBP-hydrocarbon diluent mixtures, after use and degradation in Purex type processes, are presently conditioned for reuse by washing with sodium carbonate or sodium hydroxide solutions, which may also contain potassium permanganate, followied by alkali removal by washing with dilute nitric acid. Insoluble materials and materials that are present in an aqueous phase may be removed by filtration or centrifugation. Such systems have generally been adequate for solvent recycle in existing plants, but, occasionally, it has been necessary to resort to more elaborate treatments to permit solvent recycle or to discard the major part of the plant solvent inventory. In addition to the investigation of improved treatment methods, this has led to searches for better diluents. Hanford and Savannah River are reported to have recently changed diluents to those of more paraffinic types than the spray base and Ultrasene previously used.

The products of solvent-diluent degradation are inadequately known, but acid phosphate esters, butanol, and presumably nitration products of the hydrocarbons are included. Since these products are largely higher boiling than the initial mixture, it has been obvious that a distillation separation might be much more effective than washing methods of treatment for reuse. The apparent disadvantages of distillation include greater equipment complications, probable higher cost, and the production of a residue whose disposal might be difficult.

Davis,[29] at Oak Ridge, has recently summarized work done on solvent purification by distillation. Molecular distillation readily yielded purified diluent and TBP fractions (at 35 to 70°C) from TBP-Amsco mixtures that had been degraded by Co^{60} exposure or by use in the Oak Ridge pilot plant. Davis also discussed the work of Sicilio and others[30] on rapid distillation at 0.5 mm Hg. Sicilio obtained almost quantitative recovery of materials comparable to new solvent components. The conceptual design of a 50 gal/hr plant-scale unit

for operation at 50 to 60 mm Hg was also discussed.

Electrochemical Processes

Observations of Ohse and Raub[31] suggest a possible electrochemical purification technique that is adapted to uranium in aqueous solution. It was noted that electrochemical deposition of uranium itself was thermodynamically incapable of yielding pure deposits and that the deposition of intermetallic compounds of uranium (as occurs with tungsten and molybdenum) was not a likely method for uranium purification. However, it was shown that uranium dioxide embedded in a zinc matrix could be electrodeposited from a zinc uranyl acetate bath and that a similar matrix of uranium tetrafluoride in zinc could be deposited from a uranyl acetate–zinc fluoborate bath. Copper electrodes were used with currents of the order of 2 to 5 ma/cm^2. Deposits that contained 15 to 22 per cent uranium (corresponding to 17 to 25 per cent uranium dioxide) in zinc were obtained from acetate baths that contained 40 g of uranium and 20 g of zinc per liter. Similarly, deposits that contained 46 and 35 per cent uranium (corresponding to 61 and 36 per cent uranium tetrafluoride) in a zinc matrix were obtained from fluoborate baths that contained 50 g of uranium and 50 g of zinc per liter.

Process Instrumentation

An in-line monitor that will promptly detect very small concentrations of uranium in waste

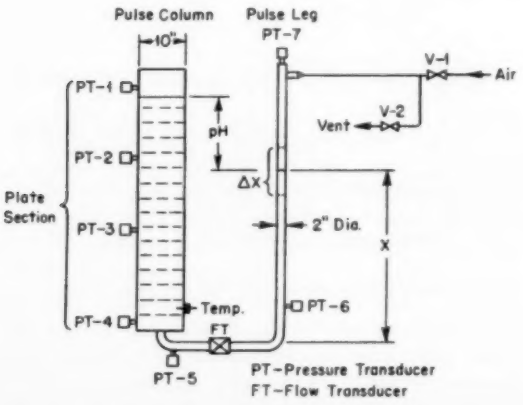

Fig. II-5 Schematic of air-pulser test system.[33]

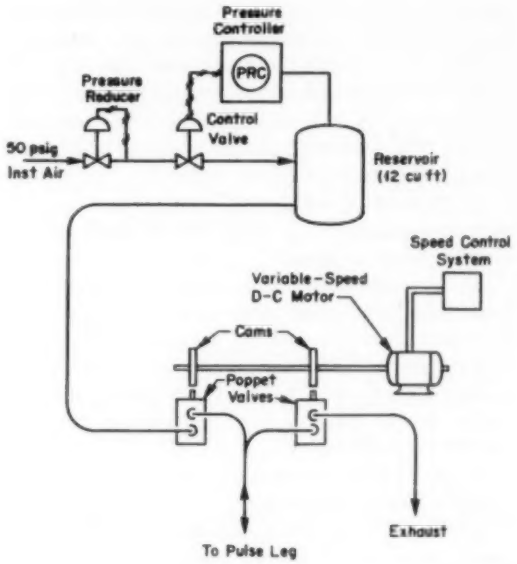

Fig. II-6 Air-pulser air-supply system.[33]

streams from a TBP plant was reported by Propst[32] at the Savannah River Laboratory. A polarograph was built and was demonstrated for detection of $10^{-5}M$ to $10^{-4}M$ uranium in synthetic process waste which was $2.2M$ in nitric acid and which contained nitrite, ferric iron, dissolved TBP, and dissolved oxygen.

Interference from ferric iron and nitrite was eliminated by the addition of ascorbic acid to the sample. TBP produced an inflection but did not affect the determination of uranium. Dissolved oxygen was removed by purging the solution with nitrogen. The complete cycle for a prototype unit was done in 10 min.

Plant Design and Operation

Pulse Columns

A program[13,33] was initiated at the Idaho Chemical Processing Plant to replace mechanical pulsers (a source of many maintenance problems and expense) with direct-air pulsers for the sieve-plate pulsed-liquid extraction columns. Figures II-5 and II-6 show, schematically, a test installation. A cold mockup was studied, and the IA column in the plant was

modified for direct-air pulsing and was successfully operated in a recent processing campaign.

Extensive studies are planned with the test installation for comparison with characteristics determined by use of an analog-computer program. The following generalizations are stated from preliminary studies:

1. Extraction efficiency was at least as good with air pulsers as with the mechanical hydraulic pulse system.
2. A much wider range of pulse-energy input was available than with existing diaphragm pulsers. Forty-five to 60 cpm represented the entire controllable frequency range for pulse amplitudes of 0.75 to 1.0 in., whereas with air pulse the IA column was operated at 100 cpm at 0.7-in. amplitudes.
3. Operating conditions were simpler and faster to set and maintain.
4. Initial costs for installed air-pulse equipment were about 12 per cent of those for the mechanical pulsers.

A report from HAPO[34] contains a good review of the history of pulse columns and brings the designs up to the present; however, since there has been much material of this nature covered by these reviews, it is only mentioned for reference.

Mixer-Settlers

Hanson and Smith of the United Kingdom Atomic Energy Authority reactor group present two concepts[35] (based on the ever-safe slab) for geometrically ever-safe mixer-settlers for high throughputs: (1) the vertically stacked design and (2) the horizontal ever-safe slab design. The vertically stacked configuration has the advantage of good hydraulic driving force, but some problems are envisaged with the construction and active operation on a plant scale. The horizontal ever-safe slab design (recommended for further development) derives a stage-to-stage driving force by use of marine propellers as mixers. Figure II-7 shows the general arrangement. It is claimed that this design permits complete independence of each stage so that no backmixing can occur. This design also allows throughputs of either phase up to the maximum without danger of a phase going over the wrong weir. Recommendation is

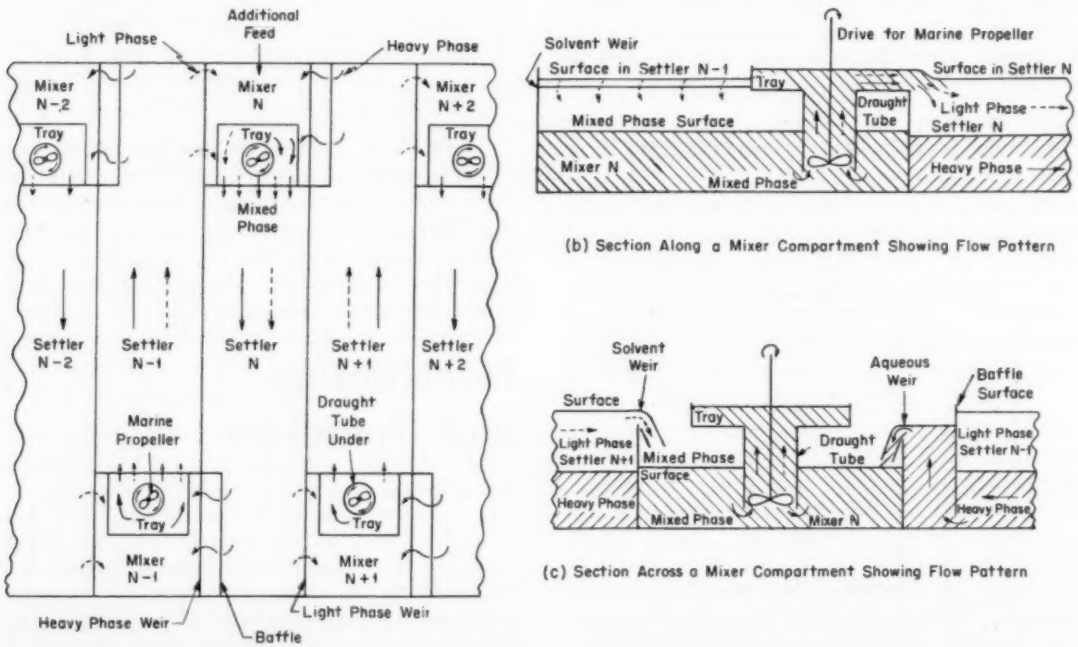

Fig. II-7 Horizontal mixer-settler.[35]

made that this horizontal type be further developed and be made available for use in future plants.

Neutron Absorbers in Storage-Vessel and Evaporator Construction

Cederberg and Buckham report[36] on mixing and evaporation in a packed vessel. This study was prompted by the possibility of using corrosion-resistant, neutron-poison packing for criticality control in tanks that are larger than the ever-safe tanks. Packings that were considered were Pyrex glass (contains boron) and boron–stainless steel alloy.

A 30-in.-diameter vessel that was packed with $\frac{1}{2}$- and $1\frac{1}{2}$-in.-diameter stoneware Raschig rings was used for the tests. For the mixing tests, tracer was introduced into 200 liters of material, and samples were taken at several points. Air-sparging times for the concentration to reach within 0.8 per cent of calculated uniform mixture were noted, and comparison was made with and without packing. The results of this work are shown in Fig. II-8. It can be noted that the $1\frac{1}{2}$-in. packing caused only a small increase in mixing time (5 to 10 fold); however, the $\frac{1}{2}$-in. packing resulted in at least a 125-fold increase in the time for complete mixing.

The evaporation tests showed little difference in rates for packing versus no packing in the vessel.

The indicated results are that a neutron-poison packing could be used in a vessel, provided that reasonable allowance is made for increase in mixing time and that one is sure that the packing would not be dissolved.

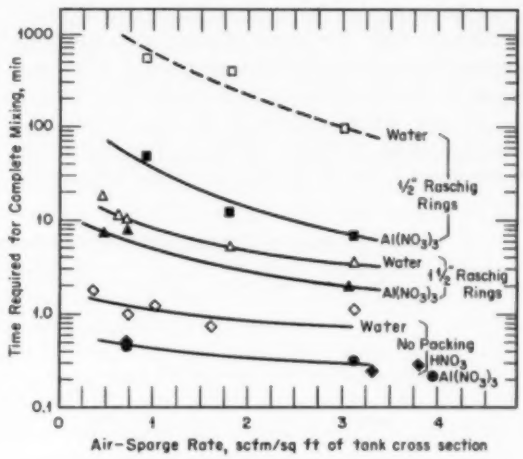

Fig. II-8 Effect of packing and sparge air on the time required to mix cupric nitrate into 2.2*M* aluminum nitrate and into water.[36]

Corrosion and Materials of Construction

The Zirflex process was developed as a head-end treatment for zirconium-matrix fuels for conventional solvent-extraction plants. Oak Ridge subsequently modified the Zirflex process by the addition of hydrogen peroxide to the dissolving medium to permit the production of homogeneous solutions when fuels with high uranium contents were used. The results of corrosion experiments with several commercial alloys in modified Zirflex solutions were reported in the January 1962 issue of *Reactor Fuel Processing*.[37] Similar tests were later made on several cobalt-base alloys and on type 347 stainless steel.[23] Some of the results of these tests are tabulated in Table II-1. The best of the group was Haynes-21, which had a surface corrosion rate of less than 0.8 mil/month over an exposure period of nearly 700 hr; however, if the observed subsurface corrosion were included, the rate would be increased to 6 mils/month. The possibility of using Haynes-21 for a dissolver that could handle stainless-steel-matrix fuels by the Darex process and zirconium-matrix fuels by the modified Zirflex process is being considered. At this point this combination appears to have certain limitations.

In a second stage of corrosion testing for the Zirflex process, two stainless steels were exposed to dissolver solutions that simulated the intermediate or terminal compositions of a dissolution. Results of these tests are also shown in Table II-1. The rates of attack for both stainless steels are higher by factors of 2 to 3 than those obtained for similar exposures in the initial dissolver solution that contained no zirconium. The increased corrosiveness of this environment is probably due to either one of two factors (or both): (1) the presence of dissolved zirconium or (2) the lower concentration of hydrogen peroxide. Maximum corrosion rate of the best alloy (type 309SCb stainless steel) was 4.5 mils/month.

At Oak Ridge the compatibility of Zirflex solutions with the construction materials in extraction equipment is being studied in an extensive series of tests with synthetic solvent-extraction feeds that might be encountered in the modified Zirflex process. The solutions were about 0.4*M* in zirconium, 3.0*M* in fluoride ion, 0.75*M* to 1.5*M* in nitric acid, and 0.6*M* to 1.0*M* in aluminum (for complexing fluoride ion).[24] The tests were conducted at 50°C. An extensive tabulation of the results for vapor-phase, interface, and solution exposure is presented in the report. Partial results of these tests are shown in Table II-2. Only results for solution exposure are shown; rates of attack for interface and vapor-phase exposure were less in all cases. Stainless-steel type 304L experienced grain-boundary attack plus some localized etching. Carpenter-20SCb suffered some intergranular attack in the heat-affected zone of the welds, particularly in the high-acid solutions. It would appear from these results that either stainless-steel type 347 or low-carbon Nionel (LCNA) would be the most useful material for construction of the solvent-extraction equipment.[23]

Table II-1 CORROSION OF VARIOUS WELDED ALLOYS IN MODIFIED BOILING ZIRFLEX DISSOLVENT[23]

Alloy	Dissolvent	Time, hr	Corrosion rate, mils/month			Comments relating to interface and solution specimens
			Vapor	Interface	Solution	
S.S. 347, welded	A*	24	0.83	4.2	4.2	Extensive edge corrosion and pitting
		500	0.67	6.4	6.3	
Haynes-21†	A*	24	0.0	0.45	1.0	
		689	0.06	0.75	0.68	
Haynes-6B, welded	A*	24	0.36	3.5	3.3	Severe weld decay and intergranular attack
		216	1.2	3.2	3.6	
Haynes-6B, solution annealed	A*	24	0.45	3.5	3.6	Severe weld decay and intergranular attack
		216	1.0	7.7	9.6	
S.S. 304L	B‡	24	0.31	13.4	14.2	Edge corrosion and pitting attack
		48	1.0	19.8	24.0	
S.S. 309SCb	B‡	24	0.36	3.7	3.6	
		48	0.36	4.5	3.9	

* A = the beginning dissolvent: 5.4*M* NH_4F, 0.33*M* NH_4NO_3, and 0.003*M* H_2O_2.

† Including localized attack, the over-all rates exceeded 6 mils/month.

‡ B = the terminal dissolver solution, which was prepared by dissolving 61 g of Zircaloy-2 in 1 liter of 5.4*M* NH_4F – 0.33*M* NH_4NO_3. The H_2O_2 concentration was about 0.001*M* H_2O_2.

A compilation of corrosion results in the various process environments of the Zircex process has been published.[23] This process involves the reaction of zirconium-matrix fuels with a variety of reagent gases to effect a separation of uranium from zirconium. Some of the results are given in Table II-3. In each of the tests involving exposure of the metal to a halogen-containing gas, duplicate specimens yielded diverse results. It was observed that the specimen of each alloy exposed in the "downstream" position of the gas stream corroded at a rate of 1.5 to 3.5 times greater than the "upstream" specimen. The reasons for this behavior are unknown. No conclusions are given in the report to indicate which of the materials tested are considered at the present time to be most useful for this processing system.

It was reported in a preceding issue of *Reactor Fuel Processing*[38] that the use of a hexavalent chromium inhibitor in strong nitric acid–hydrofluoric acid mixtures might make this solution, which is used for zirconium dissolution, compatible with titanium processing equipment. A later report[15] contains information on

the chromium inhibition of two other zirconium-dissolution media (in titanium). The first of these was a solution which is referred to as acid fluoride solution and which contains nitric acid and fluoboric acid. Reactor fuel dissolution tests (with Zircaloy-2 and Experimental Boiling-Water Reactor zirconium-uranium alloy) and simultaneous titanium corrosion tests were conducted in a large variety of solution compositions. Minimum corrosion rates were obtained with $3M$ nitric acid–$0.5M$ fluoboric acid that was inhibited with $0.3M$ ammonium dichromate. From the tabulated data presented in the report, it is evident that this solution composition also resulted in minimum ratios of corrosion rates to dissolution rates (when the corrosion rates were expressed in mils/month and the dissolution rates in mils/min, these ratios varied from 6 to 20).

The second solution in which chromium inhibition was studied was the unmodified Zirflex dissolution medium: $6M$ ammonium fluoride–$1.0M$ ammonium nitrate. When ammonium dichromate was present to the extent of $0.1M$ to $0.3M$, corrosion rates were decreased from 600 mils/month to about 5 mils/month. Corresponding dissolution rates yielded corrosion-to-dissolution ratios of 3 to 17, which corresponds rather closely to the results in the inhibited acid fluoride environments. The authors of reference 15 are concerned by the possibility that local depletions of chromate occur through the process of reduction by actively dissolving zirconium. It would be ex-

Table II-2 CORROSION OF VARIOUS ALLOYS IN SOLVENT-EXTRACTION FEEDS PREPARED FROM ZIRFLEX (MODIFIED) DISSOLVER SOLUTIONS[23]

(Temp., 50°C; Exposure Time, 336 Hr; Zr^{4+} Concentration, 0.36 to 0.49M; F^- Concentration, 2.44 to 3.33M; and Al^{3+} Concentration, 0.6 to 1.0M)

HNO_3 concentration, moles/liter	Al/F	Corrosion rate, mils/month			
		Alloy			
		S.S. 304L	S.S. 347	LCNA	Carpenter-20SCb
0.75	0.18	0.74	0.16	0.15	0.26
	0.29	0.06	0.07	0.09	0.15
	0.41	0.03	0.06	0.04	0.08
1.5	0.20	1.27	0.26	0.25	0.31
	0.26	0.19	0.22	0.15	0.46
	0.41	0.11	0.15	0.12	0.22

Table II-3 BEHAVIOR OF SEVERAL ALLOYS IN ZIRCEX PROCESS ENVIRONMENTS[23]

Gas	Temp., °C	Corrosion rate, mils/month				
		Nickel	Haynes-25	Nichrome-V	INOR-8	Pyroceram
HCl*	200		0.01	0.01	0.01	< 0.01
HCl†	350		0.25	0.16‡	0.03‡	< 0.01
HCl§	600		5.30	5.63	16.4	1.2
Cl_2¶	200	Gain	Gain	Gain	Gain	No change
Cl_2	350	0.06	0.08	< 0.01	0.08	No change
Cl_2	600	11.37 (1.1)**	35.20 (0.6)	8.79 (0.4)	27.14 (2.3)	No change
O_2††	725	0.10‡	0.02‡	0.01‡	0.01‡	0
N_2 + CCl_4¶	300		0.12	0.12	0.07	0.01
N_2 + CCl_4	450		7.3 (3.9)	1.1 (0.4)	1.2 (0.2)	0.02
N_2 + CCl_4	600		5.9 (1.2)	1.5 (0.07)	2.6 (0.13)	108
4M HNO_3	Boiling			0.17‡‡	>200§§	

* 192 hr.
† 360 hr.
‡ Rate decreased with time.
§ 34 hr.
¶ 24 hr.
** Numbers in parentheses were upstream specimens; the others were downstream.
†† 188 hr.
‡‡ 336 hr.
§§ 1.5 hr.

pected that, where local depletion occurs, highly accelerated local corrosion might also develop.

A report has been published[39] on construction materials for multipurpose head-end equipment in fuel-processing schemes. Several of the AEC production sites are striving to develop methods that are consistent with minimum capital investments for the processing of the large variety of new power-reactor fuels. One of the ways to meet this objective is to use equipment constructed of a material that is compatible with environments encountered in the processing of zirconium, stainless steel, and other types of fuels. This report covers four such processing combinations, one of which, it appears, does not really meet the requirement of a single processing line. The exception is the dual scheme that involves the Darex process in titanium and the chloride-volatility process (Zircex) in Haynes-25. The other three multipurpose processing schemes considered are (1) Darex — inhibited acid fluoride in titanium, (2) Darex — modified Zirflex in Haynes-21, and (3) Sulfex — modified Zirflex in Nionel. Considerably less information is known about the first two, and the most realistic of the three at present is the third scheme. All these systems have been discussed either in this or in past issues of *Reactor Fuel Processing*.

Both Savannah River and the Idaho Chemical Processing Plant are investigating the use of an electrolytic dissolver for dissolving both stainless-steel- and zirconium-matrix fuels. Niobium is being considered as a construction material for the cathode. A test was run at Idaho to investigate the possibility that niobium is subject to hydrogen embrittlement under cathodic conditions.[33] The test was made in an electrolytic dissolver that contained 8*M* nitric acid held at the boiling temperature. Current density was 0.5 to 1.0 amp/cm^2, and exposure time was 1000 hr. The exposed niobium cathode was analyzed for hydrogen. Comparison with an unexposed reference sample of niobium indicated that no change in hydrogen content occurred.

During the past quarter additional information was reported from two sites on the effects that accumulating corrosion products in nitric acid solution had on the corrosion of austenitic stainless steels.[12,33,40] Work at both sites is related to the development of the electrolytic dissolver. Idaho has tested four 300-series stainless steels in a simulated electrolytic dissolver solution: 1*M* nitric acid containing 75 g of electrolytically dissolved stainless steel (type 304) per liter. Titanium and Inconel were also included as test materials. Testing of Inconel was discontinued after two days because of excessively high corrosion rates. Testing of titanium was discontinued after 50 days when the rate had stabilized at a very low value. The corrosion rates of all the austenitic stainless steels started at about 1 mil/month. Rates gradually increased through the entire exposure period until after 76 days the rates ranged from 5 mils/month (type 347) to 7.2 mils/month (type 304L); the other two stainless steels (type 316 and Carpenter-20) had intermediate values. It appears from these results that, even at a nitric acid concentration as low as 1*M*, dissolved corrosion products (which include the troublesome hexavalent chromium) do have the effect of gradually increasing corrosion rates. In solutions of higher acid content, the increased rate is usually attributable to intergranular attack that occurs in grain boundaries. Microscopic examinations of coupons in the Idaho tests revealed severe pitting on the edges of the coupons and grain-boundary attack on the face of the coupons. The latter type of attack was less in stainless-steel type 347 and Carpenter-20 than in types 304L and 316.

Savannah River and Hanford have presented (graphically) the results of their work on the effect of dissolving chromium on the corrosion rate of austenitic stainless steels. These results are shown in Fig. II-9.[40] According to Savannah River, corrosion by solutions resulting from the electrolytic dissolution of stainless steel is a problem only when the solution is boiled; this is no problem during the dissolution proper. It has been their observation that, during electrolytic dissolution, chromium exists as the trivalent ion, whereas during boiling it is oxidized to the hexavalent state. Savannah River also found that the oxidation of chromium to the hexavalent state can be inhibited by the addition of nitric oxide (NO) to the solution. Additions of formaldehyde were similarly useful since they lowered the nitric acid concentration and reduced the chromate to the trivalent state.

A large number of austenitic stainless-steel coupons were exposed in a laboratory electrolytic dissolver during the dissolution of type 304

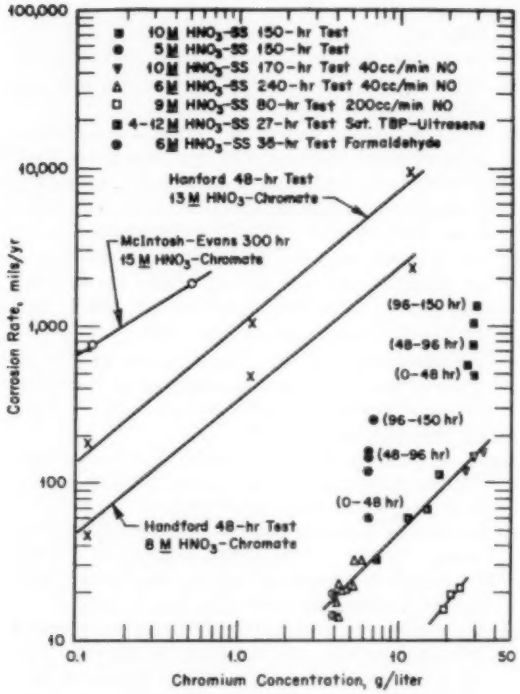

Fig. II-9 Corrosion rate of type 304L stainless steel by boiling nitric acid–chromium solutions.[40]

stainless steel. All coupons were electrically isolated from the anode and cathode of the equipment; however, considerable variations in corrosion were observed depending upon the specific position of the specimen involved. It appears difficult to locate specimens in a manner that will isolate them from current flow through the solution. Specimens that were well shielded from stray currents had corrosion rates of 1 to 3 mils/month. Specimens that were not shielded had corrosion rates that varied from 8 to 160 mils/month. Coupons that were most severely affected had large metal losses on the side of the coupon facing the cathode. In effect, this side of the specimen was dissolving anodically. This information suggests that some difficulty might be met in attempting to design the dissolver in such a way as to minimize or eliminate stray current leakage.[12]

Eleven plastics were tested by Idaho in the same boiling electrolytic dissolver solution described above. The exposure time was 96 hr. In general, fluorocarbon and polyethylene compositions were found to resist the solution. The urea, melamine, and phenol formaldehydes and the furan resins all dissolved.[12]

The precipitation of barium fluozirconate from zirconium that contained nitric acid–hydrofluoric acid dissolver solutions is considered attractive in reducing the waste volumes of the conventional Idaho Chemical Processing Plant (ICPP) process used for zirconium fuels. Room-temperature precipitations are being studied as a means of avoiding corrosion problems associated with higher temperature precipitations. Types 347Cb, 304L, and Carpenter-20Cb stainless steels were exposed at 35°C to 1*M* and 4*M* nitric acid that was saturated with barium fluozirconate. Surface corrosion rates that were observed in 15-day exposures were less than 2 mils/month for all alloys. However, Carpenter-20Cb, which suffered selective weld attack, is not recommended for use.[12]

Hanford designed and is operating a continuous critically safe dissolver for the dissolution of slags and crucibles remaining after the reduction of plutonium tetrafluoride to metal. The dissolution medium consists of 8*M* nitric acid–0.17*M* aluminum nitrate. The fluoride content of the dissolver solution builds up as the calcium fluoride crucibles dissolve. Typical final fluoride content is 0.15*M*. The dissolver is constructed of type 309SCb stainless steel, is solution annealed at 2150°F for 30 min, and is water quenched for resistance to boiling solutions of nitric acid–hydrofluoric acid solutions. The vessel was inspected after its first 50 hr of operation. A longitudinal weld showed knife-line corrosion up to 50 mils deep and 6 mils wide. Other welds showed no such local attack. The dissolver base metal, though lightly etched, still shows machine marks less than 0.5 mil deep.[41]

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

The volatilities of uranium and plutonium hexafluorides have been proposed as a basis for processing various types of irradiated nuclear reactor fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid phase–gas phase halogenation processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are employed in some of these dry halogenation processes to enhance reactor control.

On Dec. 2–7, 1961, the American Institute of Chemical Engineers, at the Fifty-fourth Annual Meeting, sponsored a symposium on volatility processing of nuclear reactor fuels. Eleven papers[1] were presented which were devoted to current volatility processes now under development. Three of the papers[1e,1f,1k] described work being done at Centre d'Étude de l'Énergie Nucléaire in Mol, Belgium, and the remainder covered work at AEC national laboratories. Although much of the information presented at the meeting has been covered in previous issues of *Reactor Fuel Processing*, some recent developments are described separately in this section.

Nitrofluor Process

The initial step in the Nitrofluor process, under development at Brookhaven National Laboratory (BNL), involves the dissolution of the reactor fuel assembly in an anhydrous NO_2-HF solution. A solution that contains 25 mole % NO_2 is capable of dissolving a wide variety of fuel-element materials at satisfactory rates over a temperature range of 100 to 200°C. Recent work[2] has been directed toward the examination of the behavior of fission products during spent-fuel dissolution in the solvent. A 50 wt.% uranium alloy that contained nine representative fission-product elements was dissolved in 20 mole % NO_2-HF solution. The nine fission-product elements that were selected (Nb, Ce, Zr, Nd, Sr, Ru, Te, Cs, and Mo) represented the important isotopes present after an average cooling time of 150 days. The results of the test dissolution showed that the rare-earth and alkaline-earth metals formed insoluble complex salts in the solvent. The alkali metals (Cs), transition metals (Zr, Nb, and Mo), and platinum metals (Ru) were soluble.

The corrosion of high-nickel alloys by NO_2-HF solutions is believed to be due to the existence of oxidizing agents such as molecular nitric acid and the nitryl ion (NO_2^+). The following reactions seem to represent the behavior of the solvent during dissolution:

$$N_2O_4 + 2HF \rightleftharpoons NO^+ + F(HF)^- + HNO_3$$

$$HNO_3 + 2HF \rightleftharpoons NO_2^+ + F(HF)^- + H_2O$$

$$H_2O + 2HF \rightleftharpoons H_3O^+ + F(HF)^-$$

$$N_2O_4 + 10HF \rightarrow NOF \cdot 3HF + NO_2F \cdot 3HF + H_2O \cdot 2HF$$

Since the compound NOF · 3HF is one of the less oxidizing constituents in the solvent, preliminary dissolution studies in this medium have been initiated.[1d,2] The compound has a boiling point of 95°C and a freezing point of 3.8°C. Dissolution studies indicated that NOF · 3HF was considerably more reactive with fuel materials than the NO_2-HF solution. Zirconium reacts at room temperature, and both uranium dioxide ceramic fuel and type 304 stainless steel dissolve about 50 per cent more rapidly in the new solvent. Monel coupons that were

exposed to NOF · 3HF at 100°C during zirconium-dissolution studies showed corrosion rates of <0.1 mil/month; both liquid- and vapor-phase coupons indicated slight etching but no pitting. Comparable data for monel in 20 mole % NO_2–80 mole % HF solution showed average corrosion rates of 8 mils/month in the liquid phase and 60 mils/month in the vapor phase; in each case severe etching and pitting were observed.

Fused-Salt Volatility Process

Hydrofluorinator Corrosion. A fused-salt fluoride-volatility process is being developed at Oak Ridge National Laboratory (ORNL) as a nonaqueous method for processing spent heterogeneous or homogeneous nuclear fuel. It is applied principally to zirconium alloy fuel elements. In this process hydrogen fluoride is bubbled through a fused-fluoride-salt bath to dissolve the alloy. The dissolved uranium tetrafluoride is transferred with the melt to another vessel in which a fluorine sparge further converts the uranium to the volatile hexafluoride. Fluoride-volatility procedures are then used to decontaminate the uranium hexafluoride product for reconversion into fresh nuclear fuel. A report has been issued[3] which summarizes the studies carried out at ORNL, Battelle Memorial Institute (BMI), and a portion of the work done at Argonne National Laboratory on corrosion associated with the hydrofluorination dissolution step in the fused-salt fluoride-volatility process. An earlier report,[4] previously reviewed,[5] has been issued on the fluorination step.

The present summary report includes scouting tests and small-scale corrosion tests and describes in detail the examination bench-scale and pilot-scale hydrofluorinators used in process development studies. The salts tested were mixtures of NaF, KF, LiF, ZrF_4, and UF_4 in various proportions. The temperature ranged from about 550 to 700°C. Emphasis has been placed on vessel analysis in which materials are subjected to processing conditions. Distinctions are made between vapor-phase, salt-phase, and interface exposure conditions. Metallographic examination was used to reveal intergranular and subsurface attack as well as dimensional changes.

From the early scouting tests on metals, high-nickel alloys appeared promising among common structural metals. Inconel was selected for 1½-in.-diameter bench-scale equipment on the basis of its well-known oxidation resistance and good mechanical properties at elevated temperatures. However, extensive corrosion losses greater than 30 mils/month were observed in all three zones of exposure. In addition, Inconel appeared to be subject to attack by selective leaching of chromium.

Nickel was first used for hydrofluorination in pilot-plant-scale vessels that were 6 in. in diameter and larger. Severe embrittlement occurred due to the presence of sulfur as an impurity in these operations. Although low rates of dimensional attack have been observed in later corrosion tests under low-sulfur conditions, nickel has been generally subject to serious intergranular attack. The safe level of sulfur and the mechanism of intergranular attack of nickel have not been established. Monel has similarly variable intergranular attack in process environments.

Copper liners have been used in pilot-plant vessels. However, wall-thickness losses of more than 50 mils/month were noted in the vapor-phase region. Subsurface scale formation was associated with internal oxidation. Very low salt-phase attack in these tests suggests possible usefulness of copper, if the effects of oxygen and certain weld defects could be excluded.

Molybdenum, gold, silver, and platinum showed promising results in small-scale tests (especially molybdenum). However, owing to the cost and fabrication disadvantages of these materials, they have not been selected for vessel fabrication. Hastelloy B (molybdenum-nickel alloy) also showed promising results, although the low ductility due to age hardening has been considered detrimental to its use. The nominal compositions of Hastelloy B and other alloys are given in Table III-1.

New nickel-molybdenum alloys not susceptible to age hardening were developed, and these were given the "INOR" designation. INOR-1, INOR-8, and Hastelloy B were given corrosion tests at BMI in simulated process environments. Approximately the same degree of resistance was shown by all three alloys, and the highest corrosion rates were exhibited at the salt-interface region. A strong temperature effect (shown in Fig. III-1) was found in these tests. Corrosion rates increased with the increased flow rate of hydrogen fluoride. On the

other hand, corrosion rates seemed to be retarded by increases in the zirconium content of all the fluoride-salt systems and by higher overpressures of hydrogen in the sodium- and zirconium-salt systems. These BMI studies concluded that INOR-8 was the most promising material for hydrofluorinator-dissolver vessels.

Table III-1 COMPOSITION OF ALLOYS USED IN BMI SCREENING TESTS[3]

Alloy	Nominal composition, wt.%									
	Ni	Cr	Fe	Mo	Co	Cu	Mn	Si	C	S
INOR-8*	70	7	5	16	0.2	0.35	0.8	0.3	0.06	0.1
INOR-1	78		0.3	20			0.5	0.5	0.01	0.01
Hastelloy B	62	1	6	28			1	1	0.12	
Inconel	72	16	8			0.5	1	0.5	0.15	0.015
Monel	67		1.5			30	1	0.1	0.15	0.01

*This alloy is commercially available from Haynes-Stellite Corp. and from the International Nickel Co.

The second pilot-plant-scale dissolver at ORNL was made of INOR-8. It was used in nine dissolutions of simulated fuel-element subassemblies that were fabricated from Zircaloy-2, and one run was made without Zircaloy-2. The average run was about 20 hr. Average wall reduction, measured with an ultrasonic thickness gauge, was 6 mils after the first four runs; no increase was shown in the next five runs. However, the final run (without the presence of zirconium metal) produced a severe pitting attack and a general wall-thickness attack. The over-all average wall-thickness reduction after the 10 runs was 18 mils maximum (at the salt interface). Pit depths up to 72 mils were noted. If run 10 is ignored, the average dissolver corrosion losses were about 0.1 mil/hr, based on hydrogen fluoride exposure time, or 23 mils/month, based on molten-salt residence time. These results show that the corrosion was more severe in the ORNL tests than in the BMI tests.

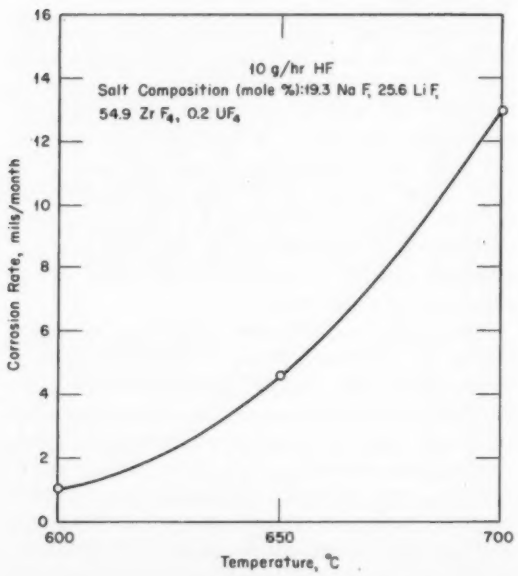

Fig. III-1 Vapor-salt-interface corrosion rates on INOR-8 at three temperatures.[3]

INOR-8 was also used in the latest ORNL pilot-plant hydrofluorinator dissolver. The original dissolution flow sheet was modified to improve the reliability of INOR-8. In particular:

1. $NaF-LiF-ZrF_4$ salt was used, thereby allowing lower temperatures to be used (about 650°C at the start of dissolution and about 500°C during the dissolution).
2. Zirconium metal was retained for the maximum possible time during hydrogen fluoride sparging.
3. A fixed vapor-salt interface region was avoided through charging and operating techniques.

Pilot-plant operations are currently under way at ORNL.

An alternate to metals for hydrofluorinator construction is provided by graphite. Corrosion tests at ANL showed very low chemical attack for graphite (less than 5 mils/month) in the process environment. Although not subject to chemical attack, graphite presents problems with respect to its porosity and fragility (relative to metals). For the above reasons, metals rather than graphite were selected for ORNL work. However, a graphite pilot-plant hydro-

fluorinator was constructed and has operated at ANL in a series of dissolutions of simulated fuel elements.

Information on the results of the graphite dissolver operation was presented in ANL reports and was previously reviewed.[6,7] The final evaluation of graphite would be expected to be affected by the development of new, low-porosity graphites and of mechanical designs adequate for specific process operations.

Recent Developments in Fused-Salt Processing. Three papers on the ORNL fused-salt process were presented at the Symposium on Volatility Reprocessing of Nuclear Reactor Fuels at the annual meeting in New York, Dec. 2 to 7, 1961.

Cathers et al.,[1a] reviewed the application of the fused-salt fluoride-volatility process to various reactor fuels. Emphasis was placed on selection of the optimum salt composition and on newer applications such as oxide fuels and stainless steel. Data from laboratory tests were presented on rates of dissolution and fluoride-product solubility in various salts for BeO, stainless steel, UO_2, UO_2-ZrO_2, and ThO_2 fuel elements. The selection of construction materials and salt compositions with respect to corrosion was discussed. Studies of the fluorination and volatilization of uranium from fused fluorides were cited. The present results were considered promising, and further work is continuing with emphasis on optimizing conditions to obtain both attractive processing rates and low vessel corrosion.

Horton et al.[1b] presented a correlation of dissolution data in the fused-salt process for the hydrofluorination of zirconium metal. Averaged rates obtained by several investigators were analyzed in terms of the following variables:

1. Hydrogen fluoride rate
2. Temperature
3. Molten-salt composition (zirconium concentration)
4. Dimensional configuration in the reactor vessel

The combined effect of temperature and salt composition was found to be well expressed in terms of the kinematic viscosity of the molten salt. The final correlation was

$$r = K\nu^a \ln \frac{w}{w_0}$$

where r = dissolution rate, lb/(hr)(sq ft of original element surface)
w = hydrogen fluoride feed rate, lb/(hr)(sq ft of reactor cross-sectional area)
w_0 = constant for particular reactor, same units as w
ν = kinematic viscosity, sq ft/hr
a = constant, found to be -2.5 to -3 in studies analyzed
K = rate constant, same units as r

Carr et al.[1c] outlined the current equipment and test runs for the ORNL fused-salt-volatility pilot plant. The pilot plant (described in previous Reviews) is being modified and evaluated in inactive runs preparatory to operation with highly irradiated, long-decayed fuel.

Dry Halogenation Processes

Several chloride-volatility processes are currently being developed for processing of reactor fuel elements. The major objective of these processes is the separation of the bulk of the structural material by volatilization from the fertile-fissile material and the recovery of the latter material in a form that is suitable for final purification. A complete description of several processes appeared in a recent Review.[5]

The Zircex process, under development at ORNL, is based on the use of hydrogen chloride, at a fuel-element temperature of 600°C, to convert the zirconium-uranium alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. This process has been extended to include treatment of uranium-molybdenum fuel and aluminum cladding.[1i,5] Recent development concerns the processing of TRIGA fuel (8 per cent uranium–91 per cent zirconium–1 per cent hydrogen, clad in aluminum, with aluminum-samarium burnable poison disks and graphite moderator plugs).[1i,8]

A major problem associated with the Zircex process is the removal of heat generated in the reaction between zirconium metal and hydrogen chloride gas. The use of a fluidized bed of inert particles[1j] to provide rapid and efficient heat transfer from the reaction zone was demonstrated at BNL. Halogenation studies on nuclear fuel-element materials were made at ANL in a two-zone fluid-bed reactor.[1k] The fuel element is first reacted with hydrogen chloride or chlorine in the lower part of the

fluidized bed to form a volatile chloride, which in turn is converted to a solid fluoride in the upper section by reaction with hydrogen fluoride. The upper zone is separated from the lower zone by a conical baffle which prevents backmixing of hydrogen fluoride into the lower reaction zone. This concept has been applied to the reaction of zirconium-uranium alloys with both chlorine and hydrogen chloride, the decladding of stainless-steel-clad uranium dioxide fuels at 600 to 640°C with chlorine, and the chlorination of uranium dioxide ceramic fuel pellets with a mixture of carbon tetrachloride and chlorine. Analyses of the inert fluid-bed particles show that the product fluorides are uniformly deposited on the surface of the fluid-bed particles.

The processing of irradiated uranium and uranium compounds which is based on the fractional sublimation of their chlorides is being studied at Mol, Belgium.[1h] Details of the process were presented in a previous Review.[5] Speechaert[1h] and Schmets[1e] described current work on the application of the process to uranium oxide and uranium carbide fuels. Uranium dioxide fuels are oxidized to U_3O_8 and then reduced to the dioxide in order to obtain a fine powder of high reactivity. The reactive uranium dioxide is converted to uranium tetrachloride by a gas-phase reaction with carbon tetrachloride. Precise control of this reaction is required to avoid formation of higher chlorides of uranium (which are volatile). The uranium values are separated from less volatile fission products by producing uranium hexachloride in the reaction of chlorine with uranium tetrachloride at 400°C.

Processing of uranium carbide fuels by this scheme essentially follows the sequence of operations described for uranium dioxide. The carbide first is oxidized to uranium dioxide with either water vapor or carbon dioxide. Carbon dioxide is preferable since no residual free carbon is retained with the uranium dioxide product.

Direct Fluorination Processes

A direct fluorination volatility process is being developed at Argonne National Laboratory (ANL)[1g] to recover uranium and plutonium from spent uranium oxide fuel elements that are clad with Zircaloy or other metals. The process consists of vapor-phase chemical decladding, direct fluorination of uranium and plutonium oxides, and separation and decontamination of the uranium hexafluoride and plutonium fluoride products. Although the dense oxide pellet fuel is not directly fluidized, fluid-bed techniques that use inert materials have been applied to aid in the removal of heat during fluorination.

Heremans and Schmets[1f] described a fluorination process for the recovery of uranium from sintered uranium oxide fuel. To conserve fluorine requirements the oxide fuel is initially converted to uranium tetrafluoride. The sintered oxide is activated by an oxidation-reduction procedure prior to conversion to uranium tetrafluoride with hydrogen fluoride. These reactions have all been studied in fluid-bed equipment. Uranium tetrafluoride is converted to uranium hexafluoride by reaction with fluorine in a fluid-bed reactor with an inert bed of aluminum oxide particles to provide a continuous inventory of fluidized solids throughout the reaction.

The direct conversion of uranium monocarbide to uranium tetrafluoride with hydrogen fluoride appears to be a promising method for carbide fuel processing.[1e] Unlike sintered uranium dioxide, sintered pellets of uranium carbide are readily reacted with hydrogen fluoride. Among the gaseous reaction products are hydrogen and various saturated hydrocarbons. Unsaturated species do not appear to be formed.

A process for the recovery of highly enriched uranium from low uranium–zirconium alloy plate fuels was developed at ANL and was demonstrated in pilot-plant-scale equipment.[9] The process involves dissolution of the fuel in aqueous hydrofluoric acid and fluid-bed drying of the solution to form the solid fluorides, followed by direct fluorination of the fluoride particles to recover uranium as uranium hexafluoride.

In the spray-drying step, the feed solution is sprayed horizontally through a two-fluid nozzle and is atomized directly in the heated fluidized bed that is composed of particles of previously dried material. The spray droplets are dried on the surface of the fluidized particles, and a dense coating is formed. Excessive particle growth was avoided by the use of air-attrition jets inserted directly in the bed. Aqueous hydrofluoric acid solutions that contained 1.2*M* to

3.6*M* zirconium, 0.007*M* to 0.03*M* uranium, and free acid concentrations from 1*M* to about 10*M* were successfully processed in a 6-in.-diameter Inconel reactor. Rates equivalent to about 3.1 kg of zirconium per hour were achieved. Experiments were successfully carried out over the temperature range from 240 to 450°C.

The granular product from the spray-drying step was subsequently fluorinated at temperatures to 600°C in fluid beds and to 700°C in static beds to remove the uranium as the volatile hexafluoride. About 90 to 95 per cent uranium removal was consistently achieved near 600°C. The relatively low uranium recovery under these conditions is a disadvantage for the application of this process to zirconium-base fuels.

Preparation and Properties of Volatile Fluorides

Preparation of Hexafluorides. Selig et al.[10] published details on technetium hexafluoride preparation, which is part of a continuing program on the preparation of transition-metal hexafluorides being conducted at ANL. Technetium metal, prepared by reducing dry NH_4TcO_4 with hydrogen at 600°C, was reacted for 2 hr with excess fluorine in a closed nickel vessel at 400°C. The volatile product was purified by fractional sublimation. At room temperature the hexafluoride is a golden-yellow solid. The melting point determined in a capillary was 33°C. X-ray-diffraction studies have shown that the solid undergoes a solid-solid transition at about −3.5°C.

Workers at ANL have also reported the preparation of platinum hexafluoride, which is the first hexavalent compound of platinum that has been formed with a monovalent element.[11] The compound was prepared by burning a platinum wire at an estimated temperature of 1000°C in a fluorine atmosphere. Solid platinum hexafluoride has a transition point at 3.0°C (32.5 mm Hg pressure) and a fusion point at 61.3°C (586 mm Hg pressure). The liquid boils at 69.14°C.

Platinum hexafluoride is the most reactive and least stable of the known hexafluorides. Experiments were performed which indicated that it was possible to produce plutonium hexafluoride from plutonium tetrafluoride by the use of platinum hexafluoride as a fluorinating agent. Platinum hexafluoride was also effective in producing bromine pentafluoride from bromine trifluoride.

Although platinum hexafluoride is quite unstable, the rate of thermal decomposition into fluorine and a lower platinum fluoride is negligible at room temperature. Only slight decomposition was observed after heating 1 hr at 145 to 165°C.

Kinetics of Plutonium Hexafluoride Decomposition and Other Literature. The direct fluorination volatility process is being developed at ANL to recover uranium and plutonium from spent uranium dioxide power-reactor fuels. After the cladding is removed, the fuel is treated with fluorine to convert the oxides to the respective fluorides. Uranium hexafluoride is relatively stable at elevated temperatures, whereas plutonium hexafluoride undergoes thermal decomposition to plutonium tetrafluoride and fluorine. Knowledge of the equilibrium constant and rate of thermal decomposition of plutonium hexafluoride is essential to avoid decomposition during transport of the gas through heated zones.

J. Fischer et al.[12] published results on the rates of thermal decomposition of plutonium hexafluoride. Studies made in both static and flow systems show that the rate is dependent both on the surface area of the plutonium tetrafluoride produced and on the pressure of plutonium hexafluoride. Experimental results on the thermal decomposition were fitted to a rate equation which assumes concurrent first and zero orders with respect to plutonium hexafluoride pressure. The first-order dependence was attributed to unimolecular, homogeneous decomposition of plutonium hexafluoride in the gas phase, and the zero-order dependence was attributed to simultaneous, heterogeneous decomposition of plutonium hexafluoride on the surface of plutonium tetrafluoride saturated by chemically adsorbed gas.

Reference 13 is a general review of the properties and methods of preparation of the fluorides of the actinide elements. Over 230 references are cited with specific coverage on thorium, uranium, and plutonium fluoride.

Pyrometallurgical Processing

Development of pyrometallurgical processes is being pursued at several sites in the anticipa-

Fig. III-2 EBR-II complex. (The fuel-cycle facility, with its 200-ft stack for controlled discharge of gases suspected of being radioactive, is adjacent to the shell that houses the EBR-II reactor.)

tion that processing economies will result (1) from the capability of such processes for handling short-cooled fuels with an attendant reduction of fuel inventories, (2) from the avoidance of chemical conversions, and (3) from the general simplicity of the processes. Development of these processes has accompanied the development of fast reactors. The high fissionable-material content of the fuels for fast reactors and the necessity of processing the fuels many times before complete fuel consumption is realized make necessary the development of simple, economical processes for such fuels.

Melt Refining

Of various pyrometallurgical processes, the melt-refining process (a simple melting process in which fission products are removed by volatilization and selective oxidation reactions) is in the most advanced state of development. Its development has been accelerated because it will be used for recovery of enriched uranium from the first core loading of the Experimental Breeder Reactor No. 2 (EBR-II). For this purpose a fuel-cycle facility has been constructed adjacent to the reactor, which is located at the National Reactor Testing Station in Idaho. Figure III-2 shows an aerial view of the EBR-II complex. The analytical and service building is in the foreground. The fuel-cycle facility, with its concrete shielding extending above the roof line of the remainder of the building, is adjacent to the shell that houses the EBR-II reactor. The 200-ft stack that towers over the fuel-cycle facility will be used for the controlled discharge of gases that are suspected of being radioactive. Operation of this reactor and processing facility will start within the next year.

The status of construction of the fuel-cycle facility and of equipment items that have been or are to be installed in this facility is discussed in the latest progress report of the Argonne Chemical Engineering Division.[14] Included in the material and equipment items are processing equipment, cranes and manipulators, radiation-resistant lubricants, and an integrating glass dosimeter that will be used in the processing facility. A measuring procedure using glass dosimeters has been established which permits determinations of gamma exposures in the range of 10^5 to 10^9 rads to an accuracy of ±20 per cent.

Four experiments were made at ANL to demonstrate the melt-refining process at nearly full plant-scale activity levels. All experiments showed essentially complete removal of the rare gases, the rare-earth elements, and yttrium, barium, strontium, iodine, and tellurium but no removal of ruthenium and molybdenum. Zirconium was removed to a slight extent (approximately 10 per cent), probably as a result of carbon contamination. The fates of the fission products that were removed were ascertained in the fourth experiment.[14] It was found that the rare earths, yttrium, and tellurium were largely concentrated in the melt-refining skull, whereas substantial portions of the barium and strontium migrated into the walls of the zirconium oxide crucible. No preferential removal of molybdenum or plutonium from the metal phase occurred. Radiochemical analyses of nickel specimens suspended above the melt-refining furnace showed cesium, iodine, barium, and strontium to be the principal condensable fission-product species volatilized during melt refining.

The melt-refining process was discussed along with other pyrometallurgical processes in a paper presented at the 1961 Winter Meeting of the American Nuclear Society.[15] Also presented at this meeting was a paper on the fission-gas release and swelling of the EBR-II uranium-fissium pins during melt-refining operations.[16] Fission-gas release was slow when the pins were heated below 750°C: less than 0.1 per cent of the xenon and krypton evolved in a $1\frac{1}{2}$-hr heating period. Above 750°C the evolution rate was rapid: more than 98 per cent of the gas evolved by the time the alloy was fully melted at 1090°C. No significant difference was noted in the behavior of xenon and krypton. A sharp increase in diameter of the uranium-fissium pin also occurred at about 750°C. The diameter continued to increase with further heating, and a maximum diametral increase of 47 per cent was reached at about 1000°C.

A study was made of the phase relations and the properties of the EBR-II uranium-fissium alloys which bracket the composition chosen for the first core loading of the EBR-II reactor.[17] A method of analysis of such alloys by optical emission spectroscopy has also been reported.[18]

Fundamental Studies of Liquid-Metal and Salt Solutions

Solubilities in Liquid-Metal Systems. The solubilities of metals whose separation is being attempted are of prime importance in the design of fuel-processing methods. The solubilities of zirconium, niobium, molybdenum, palladium, and thorium in liquid zinc in the temperature range of 420 to 1000°C were recently published.[19] The solubilities of vanadium and praseodymium have also been reported.[14]

The changes in uranium solubility with magnesium concentration in zinc are utilized in several liquid-metal processes under development at ANL. The effect of the magnesium concentration on uranium solubility is illustrated in Fig. III-3. A maximum in the uranium solubility occurs at an intermediate magnesium concentration that depends on the temperature. At high magnesium concentrations the uranium solubility becomes very low. Thus the uranium solubility in magnesium-zinc systems can be varied between wide limits by varying the magnesium concentration.

In Fig. III-3 the primary field of crystallization to the left of the peak solubility down to a temperature of about 600°C is the delta uranium-zinc intermetallic compound (U_2Zn_{17}). The equilibrium solid phase in the area to the right of the peak solubility is uranium.

Nature and Thermodynamic Properties of Metals and Intermetallic Compounds. In the solubility studies in references 14 and 19, the nature of the intermetallic compound in equilibrium with the saturated melt was often identified or tentatively identified. The intermetallic compounds in the praseodymium-cad-

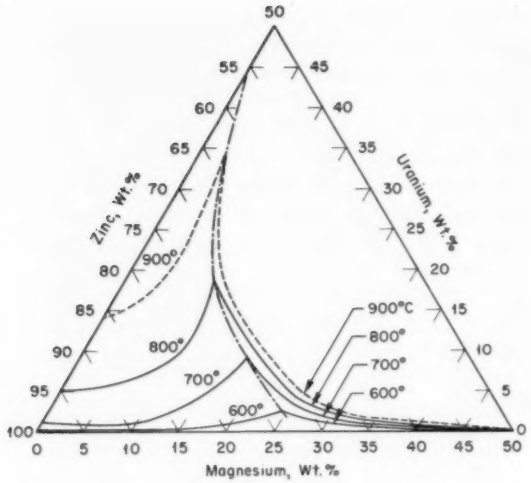

Fig. III-3 The solubility of uranium in zinc-magnesium melts.[14] (Isothermal and peak solubility lines are shown.)

mium system have been identified by effusion studies.[14] Distinct phases that were identified were $PrCd_{11}$, Pr_2Cd_9, and $PrCd_2$. A phase was found with a range of homogeneity extending from $PrCd_{\sim 5.5}$ to $PrCd_{\sim 6.5}$, and a wide solid solution range was found between $PrCd_{3.1}$ and $PrCd_{4.2}$. The crystal structures of thorium-lead and uranium-lead intermetallic compounds have been determined.[20]

Phase diagrams have been constructed for the lanthanum-cerium and lanthanum-calcium systems.[21] Lanthanum and cerium are mutually soluble in both liquid and solid states. An immiscibility gap exists in the lanthanum-calcium system.

In a continuing program at Mound Laboratory, the physical properties of various metals and alloys associated with reactor fuel systems are being determined. The density of liquid lanthanum was determined from 940 to 1000°C by the vacuum pycnometer method. The results[22] are shown in Fig. III-4. Also shown in Fig. III-4 are four values determined at Ames Laboratory (Report ISC-659) in which the sessile drop method was used. From thermal-expansion coefficients an estimate of 1.7 per cent was made for the volume expansion occurring on fusion of solid lanthanum.

The liquid range of liquid metals and some of their physical properties have been reported,[23] both to coordinate available data and to encourage research in areas where data are missing. Among the properties discussed were self-diffusivity, chemistry of liquid metals, viscosity, critical properties, and ohmic heating. Self-diffusivity measurements in liquid tin[24] have been carried out between 250 and 1000°C. A theory by which surface tensions of molten metals can be calculated has been proposed.[25] An empirical surface tension-temperature relation for liquid metals has been published.[26] The current literature on liquid metals is periodically reviewed by the MSA Research Corporation. The eighteenth of a series of abstract bulletins on liquid-metals technology was recently issued.[27] A compilation of 35 papers that deal with the physical chemistry of liquid-metal systems has also been published.[28]

Distribution of Elements Between Immiscible Phases. Studies of the distribution of fissionable and fission-product elements between immiscible phases are being made in order to evaluate solvent-extraction possibilities. The codistribution data for uranium, cerium, ruthenium, and plutonium between lead and zinc have been measured[14] and are presented in Fig. III-5. Previous single-solute data for cerium and uranium agree well with the multiple-solute data.

The effect of extractant alloy composition on the distribution of plutonium and various fission products between a uranium–5 wt.% chromium eutectic phase and a magnesium-silver alloy has been explored at Ames.[29] The results showed an increase in the extraction of plutonium as the composition of the alloy approached

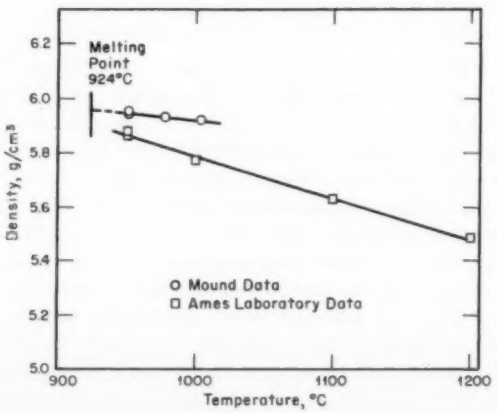

Fig. III-4 Density of liquid lanthanum.[22]

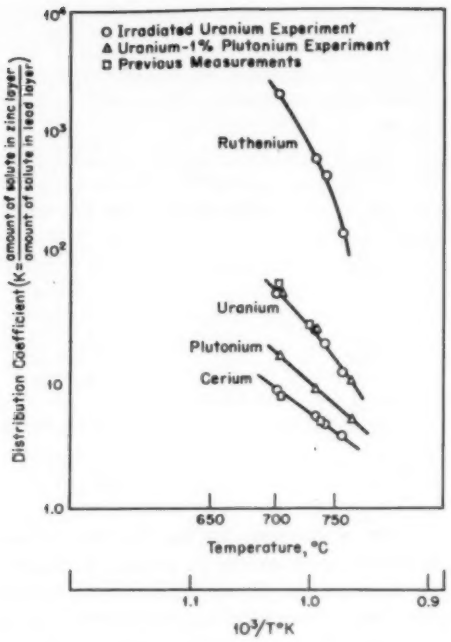

Fig. III-5 Codistribution of uranium, cerium, ruthenium, and plutonium between lead and zinc as a function of temperature.[14]

pure silver. Complete extraction of plutonium can be readily achieved. Yttrium, cerium, barium, and strontium had fairly high distribution coefficients in favor of the extractant alloy at all compositions of the alloy. Zirconium distributed preferentially into the uranium phase.

Reduction of Compounds in Liquid-Metal Systems. The reduction of compounds, particularly those of plutonium and uranium, is necessary in several pyrometallurgical processes. A study was recently conducted on the equilibrium-controlled reduction of uranium chloride in an alumina–fused salt system composed of aluminum and potassium chlorides.[30] It was concluded that molten aluminum chloride–potassium chloride constitutes a salt system of practical and theoretical interest. By changing the mole ratio of the two salt constituents, marked variations in the reduction of uranium trichloride were demonstrated. These were attributed to changes in the chloride ion activity and to equilibria in the salt system involving complex ions.

The reduction of uranium oxides by magnesium in zinc-magnesium–molten salt systems was discussed at the 1961 Winter Meeting of the American Nuclear Society (ANS).[31] Advantages offered by the use of a molten salt were (1) a marked increase in reduction rate, (2) scavenging of the magnesium oxide by-product by the molten-salt flux, and (3) ability to conduct reductions in an air atmosphere. The effect of salt-flux composition on the reduction of U_3O_8 is shown in Table III-2. Two general conclusions were drawn from these data: (1) rapid and complete reductions of U_3O_8 can be achieved with certain fluxes in an air atmosphere, using simple equipment; and (2) a systematic relation exists between the effectiveness of reductions and the atomic weights of

Table III-2 EFFECT*[31] OF FLUX COMPOSITION ON THE REDUCTION OF U_3O_8

Flux composition			Per cent reduction at time indicated				
47.5 mole %	47.5 mole %	5.0 mole %	10 min	20 min	30 min	60 min	120 min
LiCl	$MgCl_2$	MgF_2	99.4	99.4	99.9+	99.9+	99.9+
NaCl	$MgCl_2$	MgF_2	86.0	99.4	99.4	99.4	99.4
KCl	$MgCl_2$	MgF_2	70.5	90.9	97.8	97.0	98.0
LiCl	$CaCl_2$	MgF_2	26.7	44.0	56.0	86.0	99.8
LiCl	$SrCl_2$	MgF_2	25.1	42.0	59.4	95.0	96.0
LiCl	$BaCl_2$	MgF_2	12.5	21.6	26.0	52.0	85.0
LiCl	NaCl	MgF_2	5.7	9.0	8.8	13.3	23.4
$CaCl_2$	$MgCl_2$	MgF_2	97.0	99.0+	99.0+	99.0+	99.0+
$MgCl_2$	$MgCl_2$	MgF_2	97.5	99.9+	99.9+	99.9+	99.9+

* Conditions: Metal phase, 400 g of Zn–5 wt.% Mg; flux phase, 200 g as indicated; oxide, 4.7 g of U_3O_8, −325 mesh; atmosphere, air; temperature, 750°C; mixing rate, 800 rpm; crucible, alumina; agitator, quartz. Theoretical uranium concentration in metal phase at 100% reduction: 1.0 wt.%.

alkali and alkaline-earth cations present in the flux, the most effective reductions occurring with the lighter cations. An alkaline-earth halide is necessary for successful reductions. Magnesium chloride is the most effective of the alkaline-earth halides.

In the same paper[31] it was observed that complete reductions of thorium oxide had been achieved in the presence of molten-salt fluxes of suitable composition. Although the reduction rates of thorium dioxide were slower than those of U_3O_8, the same general relations between reduction rate and flux composition were observed. Additional information on the reduction of uranium and thorium oxides by magnesium in flux metal systems has subsequently been reported.[14] It has been found that the magnesium cation concentration of the flux must not be lower than 10 to 20 mole % of the total cations if complete reduction of U_3O_8 is to be achieved in a practical period of time. With proper choice of flux composition, complete reductions of thorium dioxide by zinc–5 wt.% magnesium solutions were achieved in 3 hr at 750°C.

Development of Liquid-Metal and Salt Processes

A number of fuel-recovery processes now under development utilize molten metals and salts as processing media. Most of these processes were reviewed in a paper presented at the 1961 Winter Meeting of the ANS.[15] All the processes have been discussed from time to time in these reviews.

Development continues at ANL in liquid-metal processes to be incorporated into the EBR-II fuel cycle, namely, a process for reclaiming uranium from crucible residues of the melt-refining process and a process for isolating plutonium from the EBR-II blanket material.[14] Both processes have been demonstrated in small-scale runs, and plans are now being made to scale the processes up to nearly full plant scale.

In the EBR-II blanket process, the plutonium is separated from uranium in a magnesium-rich zinc solution. Attention is now being turned to isolation of the plutonium from this solution. Although evaporation of the magnesium and zinc appears to be a straightforward procedure, attention is also being given to other plutonium-concentration procedures such as the precipitation of the plutonium as the hydride which could be later decomposed to metal. In a preliminary experiment 70 to 75 per cent of the plutonium was precipitated as the hydride from a 50 per cent magnesium–zinc solution, which initially contained 0.1 wt.% plutonium, at a hydrogen overpressure of 2 atm.

Table III-3 DISTRIBUTION OF CERIUM, YTTRIUM, AND PROTACTINIUM BETWEEN MOLTEN MAGNESIUM–38 WT.% THORIUM ALLOY AND POTASSIUM CHLORIDE–LITHIUM CHLORIDE EUTECTIC CONTAINING MAGNESIUM CHLORIDE[29]

Temp., °C	Conc. of $MgCl_2$ in salt, wt.%	Component and no. of equilibrations	Distribution coefficient (wt.% in salt/wt.% in metal)
700	5.0	Ce, 2	0.8 ± 0.2
700	15.0	Ce, 2	2.5 ± 0.1
800	15.0	Ce, 5	1.9 ± 0.1
600	15.0	Y, 3	7.5 ± 0.8
700	15.0	Pa,* 1	2.0×10^{-3}
650	20.0	Pa,* 1	0.76×10^{-3}
650	†	Pa,* 1	3.4×10^{-3}

* Distribution coefficient cpm/g in salt divided by cpm/g in metal.

† Salt composition NaCl–48 mole % $MgCl_2$ (m.p. 450°C).

Pyrometallurgical processes for the separation of thorium from uranium are under study at Ames Laboratory. In one of these processes, the uranium is precipitated out of solution while the thorium is being dissolved to produce a 38 wt.% thorium–magnesium alloy. Studies are under way at Ames on the removal of fission products from the magnesium-thorium solution by extraction into a potassium chloride–lithium chloride eutectic that contains 15 per cent magnesium chloride.[29] The distribution coefficients for cerium and yttrium in favor of the salt phase are not large (see Table III-3), whereas protactinium strongly distributes into the metal phase. A cyclic procedure has been suggested in which cerium and yttrium are removed from the separated salt phase by reduction with magnesium in a 3 wt.% magnesium–zinc alloy. The scrubbed salt can then be returned to the magnesium-thorium solution and the cycle repeated until sufficient extraction of fission products has been realized.

Construction Materials

Materials evaluation studies are in progress to evaluate the compatibility of various materials with the liquid-metal–fused-salt sys-

tems of the types contemplated for processing reactor fuels. Pressed-and-sintered beryllia crucibles (4 in. in outside diameter by 9 in. high) continue to show promise for the precipitation and retorting steps of the skull reclamation process.[14] In the final or retorting step, residual solvent metals are vaporized from the uranium product. In recent runs in the beryllia crucibles, over 99 per cent of the uranium product has been readily dumped from the crucible as well-agglomerated masses. However, in the course of use of the beryllia crucibles, hairline cracks have developed. Although in small-scale experimental work these cracks have posed no problems even on continued reuse of the crucibles, there is concern about the possibility of eventual crucible failure as a result of hairline cracking, particularly on extrapolation to plant size. Therefore a design is being developed which will minimize the consequences of crucible cracking. A tungsten crucible was unsatisfactory for retorting because the uranium product adhered to the crucible. Additional solution-stability runs at ANL have shown very good stability of uranium-magnesium-zinc solutions in tungsten crucibles.[14] Because of this and the inertness of tungsten to corrosion by the magnesium-zinc–fused salt systems, the problem of finding the most suitable means of fabricating tungsten crucibles is being studied. Several means appear to be feasible, but the two most promising methods are: (1) isostatically pressing tungsten powder followed by sintering and (2) plasma-arc spraying tungsten powder on a mandrel followed by sintering. Fabrication of tungsten accessories, such as agitators, is also under study. Vapor-deposited tungsten coatings on stainless steel, molybdenum, tantalum, Pyroceram, mullite, and graphite were tested by thermal cycling between 800 and 100°C. All coatings flaked or peeled with the exception of that on graphite where a strong tungsten-carbon bond seems to have formed.

In additional corrosion work at ANL,[14] a 30 per cent tungsten–molybdenum alloy appeared by metallographic examination to be unattacked by zinc, zinc–5 per cent magnesium, and zinc–50 per cent magnesium at 850°C. Boron nitride failed in zinc-magnesium systems. Additional data are reported on the corrosion of type 405 stainless steel by cadmium-magnesium-zinc systems.

Factors affecting the corrosion resistance of tantalum to molten-plutonium Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) alloy fuels are being investigated at Los Alamos. A postulated effect of traces of calcium and magnesium in a plutonium-iron fuel alloy in causing intergranular penetration of the tantalum container was confirmed.[32] Through control of these impurities, an adequate container lifetime for LAMPRE operation at temperatures up to 650°C seems assured. At higher temperatures, however, solution attack of tantalum is known to occur. To control this solution attack, carbon or silicon is being added to the alloy.[32,33] The use of high annealing temperatures (up to 1450°C) for tantalum capsules has also been found to provide a major improvement in the corrosion resistance. The capsules used for the first loading of the LAMPRE-I reactor were annealed at 1300°C. The reactor loading has now been melted for 3600 hr, mostly at 480°C, with excursions in central capsules up to 525°C during operating periods. Two capsules that were removed and examined metallographically showed no signs of attack.

Fourteen capsules that were made from experimental alloys produced at Los Alamos Scientific Laboratory[33] have been under test for 2100 hr at 625°C. The alloys contain various amounts of tungsten, thorium, yttrium, or hafnium. No corrosion failures have been experienced, and these alloys are judged to be at least equal to tantalum in corrosion resistance. Exposures to plutonium alloys will be made at higher temperatures to determine whether the materials are superior to pure tantalum.

Development of Equipment and Techniques

The use of autoradiography to investigate a number of problems concerning the distribution of uranium and other radioactive elements has been described.[34] Examples are given of the use of macro- and high-resolution methods for determining the behavior of trace quantities of materials that cannot be detected by metallographic methods.

Other Nonaqueous Processes

Pyrochemical processing techniques, which have been proposed principally for oxide and

carbide fuels, are characterized by high-temperature procedures involving gases, molten salts, or liquid metals as reagents and media for reactions. The pyrochemical processing techniques are similar to the pyrometallurgical processes in capability for handling short-cooled fuels, in simplicity, and in compactness. Since only moderate fission-product decontamination is realized in both types of processes, they are usually integrated with remote fuel-fabrication procedures to form a complete fuel cycle.

Oxide Fuel Processing

The salt-cycle process currently being developed at Hanford is an electrolytic procedure for processing irradiated uranium oxide–plutonium oxide fuels.[35–38] The mixed oxide fuel is dissolved in a molten chloride salt by sparging the mixture with chlorine or hydrogen chloride. A portion of the uranium in solution is reduced cathodically to the dioxide, which is essentially free of plutonium and is a by-product of the process. The plutonium and remaining uranium are then codeposited as the dioxides. This product is thereby enriched sufficiently in plutonium that it can be recycled to the reactor.

Studies of uranium dioxide dissolution rates in various molten chloride salts sparged with chlorine have shown more consistent data with large, single specimens than with the powdered material.[37] Short-term (10-min) exposures indicated a rate of 0.25 mg of U/(cm^2 of uranium dioxide surface area)(min) in the following salt systems: NaCl-KCl at 700°C; $MgCl_2$–1.5 KCl at 600°C; and $PbCl_2$–2.5 KCl at 600 and 700°C. In the last salt system, the rate was reduced somewhat as the proportion of potassium chloride was decreased. Longer-term measurements show increasing rates, probably as a result of catalysis by an increasing uranyl chloride concentration. The rate appears to be proportional to the one-half power of uranyl chloride concentration. Striking increases in the rate were produced by small additions of thallium, iron, and copper chlorides. A maximum in the rate in the vicinity of 600°C is reported for the thallium chloride-catalyzed reaction.

Experimental results on the dissolution of uranium dioxide in low-temperature melts by hydrogen chloride sparging indicate that different U(IV) species are formed in lithium chloride–potassium chloride and magnesium chloride–potassium chloride.[36] Subsequent oxidation by sparging with air progressed at rates differing by a factor of 2 in the two salt systems, thereby lending additional weight to the thesis that two different species are present.

Table III-4 SOLUBILITIES OF CHLORINE AND HYDROGEN CHLORIDE IN SELECTED MOLTEN SALTS[36]

Salt system and mole ratio	Approximate melting point, °C	Temp., °C	Solubility, ppm	
			Cl_2	HCl
KCl-NaCl, 1:1	667	800	63	50
		700	53	79
KCl-$MgCl_2$, 3:2	450	600	35	101
		500	28	135
KCl-$PbCl_2$, 2.5:1	585	700	20	
		600	14	

The solubilities of chlorine and hydrogen chloride in molten chloride systems have been determined,[36] and the results are presented in Table III-4. It is of particular interest to note that, in each case, the chlorine solubility increased with temperature. The potassium chloride–lead chloride system showed the least tendency to dissolve chlorine. It was noted that removal of chlorine or hydrogen chloride by helium sparging was considerably slower in the potassium chloride–magnesium chloride melt, which suggests that some type of bonding with the magnesium chloride occurred.

Investigation has continued on the cathodic reduction of uranium dioxide from molten chloride salt media.[35–38] Using the potassium chloride–lead chloride system, single crystals of uranium dioxide weighing up to 4 g have been prepared. The melt contained 25 wt.% uranium as uranyl chloride initially, and it was thoroughly dried by chlorine sparging and anodic treatment. The number of crystals formed was controlled by a quartz shroud with 1-mm holes surrounding the cathode. The product crystals had an oxygen-to-uranium ratio of 2.002 and contained 50 ppm lead and 200 ppm potassium. Breaking up agglomerated crystals prior to washing proved highly effective in reducing their lead content.

Analysis of time-lapse infrared photographs made during the deposition confirmed the following conclusions:

1. All of the identifiable crystal faces (1 1 0, 1 0 0, and 1 1 1) grow at approximately the same rate, at least in the later stages of growth.
2. As would be expected, the crystal angles do not change measurably during growth.
3. The crystals reaching the shroud were sufficiently small that several progressed through each hole in the shroud.
4. Many crystals branched quite rapidly immediately after growing through the holes.
5. Once this initial branching ceased, no branching occurred during the remainder of the run (perhaps as much as 95 per cent of the run). In fact, there is some evidence of fusion (the elimination of crystal boundaries) in the later stages of the run.

In general, the prime requirement for growing large uranium dioxide crystals is a dry, oxygen-free system.

The crystal growth characteristics seem to depend on the uranium concentration in the melt.[36] In an experiment in which the uranium concentration was reduced continuously from 20 to 1 wt.%, crystal growth was good in the early stages, some branching was observed at 10 wt.%, and the deposit at the end of the run was a fine powder.

An equimolar lithium chloride–potassium chloride melt also appears to be suitable for the growth of large, ceramic-grade uranium dioxide crystals. This melt has the advantages of less volatility and a lower density than the potassium chloride–lead chloride system.

A new technique which utilizes an impedance bridge has confirmed earlier chronopotentiometric data which showed the reduction of uranyl chloride to uranium dioxide to proceed by a two-step mechanism involving U(V) as an intermediate species.[37,38]

Previous work has demonstrated the feasibility of electrodepositing plutonium-free uranium dioxide and of codepositing uranium and plutonium oxides, depending on the conditions employed. To add flexibility to the salt-cycle process, it would also be desirable to recover uranium-free plutonium. Preliminary studies in which melts that contained uranium and plutonium were sparged with dry oxygen did not produce encouraging results.

The separation of rare-earth fission products from plutonium is also of interest since these products represent a serious source of nuclear poisons. By substituting lithium chloride–potassium chloride for the sodium chloride–potassium chloride system, the plutonium–rare earth separation factor was raised from 6 or 7 to 250. In the lower melting systems, the predominant valence state of plutonium can be raised from (III) to (IV) by the addition of chlorine; the separation from trivalent rare earths is thereby made easier.

Engineering work reported on the salt-cycle process has been concerned mainly with the electrodeposition of large batches (up to about 100 lb) of uranium dioxide.[35,36] The salt solution is prepared by dissolving U_3O_8 to produce 15 to 20 wt.% uranium by chlorine sparging at 700°C. An 80-liter bath of lead chloride–potassium chloride (mole ratio 1 : 2.5) is used. The electrolysis proceeds at a rate of about 2.5 lb of uranium dioxide per hour with a current efficiency of 82 per cent. The importance of dry melts in achieving good deposits is emphasized.

At Atomics International[39–41] preparations are being made to demonstrate, on a 100-g scale, the remote refabrication of irradiated uranium dioxide fuels that have been processed by the low-decontamination oxidation-reduction process. This process consists of alternate oxidation and reduction of the fuel by oxygen and hydrogen until the particle size is reduced sufficiently for refabrication. Fission-product removals achieved by this procedure are small, the principal objective being to facilitate reenrichment and refabrication of the irradiated fuel. During inactive testing of the remote refabrication equipment, enriched uranium dioxide pellets have been prepared for use as reactivity standards.

A report has been issued[42] in which oxidative decanning of irradiated uranium dioxide (15,000 Mwd/metric ton of uranium) was described. The irradiation had no detrimental effect on the process. The optimum rate was found at 465°C and 15 in. Hg (absolute) oxygen pressure, and it was increased by a factor of 8 to 10 by perforating the stainless-steel cans that contained the uranium dioxide.

Carbide Fuel Processing

Three potential processes for the recovery of uranium carbide fuels are under development at Atomics International.[39–42] The first is a simple carbide-oxide-carbide cycle in which the uranium carbide fuel is first converted to uranium oxide by treatment with oxygen. The uranium carbide is then regenerated by carbo-

thermic reduction. The oxidation step is currently being scaled up to handle kilogram quantities of uranium monocarbide. Experimental work has also been reported on the possible use of a fluidized bed of aluminum oxide in the air oxidation of uranium carbide.[39,40,43] The reaction rate can be readily controlled by regulating the flow of air. In the Atomics International work,[39,40] the uranium oxide carried from the bed was collected by a cyclone separator that was backed up with a filter.

Further kinetic studies of the reduction step confirmed a second-order rate law for the uranium dioxide–carbon reaction

$$\frac{x}{1-x} = kt$$

where x is the fraction of the total carbon monoxide evolved in time t. When pelletized reactants were used, k tended to decrease abruptly when x reached a value of about 0.9, whereas k remained constant at x values exceeding 0.95 in most of the experiments with powdered reactants. A least-squares equation for k based on 32 experimental determinations is

$$\log k = 9.82 - \frac{16{,}080}{T} \pm 0.20 \text{ (rms error)}$$

Although some variation occurred in the absolute values of k, the temperature dependence of the reaction was consistent. In general, when pellets were used, the reaction reached 90 per cent completion in 1 hr at 1500°C and 95 per cent completion in 1 hr at 1700°C. With powdered reactants the reaction required about 2 hr at 1500°C for 90 per cent completion. Carbon analyses on the uranium carbide product varied from 4.39 to 5.20 wt.%, with most of the results falling in the vicinity of 4.80 wt.%, the theoretical figure for uranium monocarbide. The carbon-content data agree reasonably well with results predicted from weight-loss information. The indications are that the carbon content can be controlled to ±0.15 wt.% when an operator has gained sufficient familiarity with the process operations and equipment.

The second carbide fuel process under investigation at Atomics International[39–41] is an electrolytic reduction of uranium carbide in a lithium chloride–potassium chloride bath, metallic uranium being deposited on a molybdenum cathode. The uranium deposit is dissolved in mercury, the mercury is removed by distillation, and the uranium deposit is then converted to uranium carbide by reaction with propane.

The electrolytic-dissolution technique for uranium carbide also appears to be suitable for the removal of stainless-steel cladding. Uranium monocarbide that was clad with 10-mil stainless steel was subjected to anodic dissolution in a lithium chloride–potassium chloride–uranium tetrafluoride salt bath. The cladding material was corroded through, and some carbide was dissolved with a current efficiency near 100 per cent.

Some fission-product decontamination data have recently become available on the electrolytic method:

Fission-product element	Decontamination factor (average of six experiments)
Barium	3000
Strontium	5000
Rare earths	700
Cerium	66
Ruthenium	500
Zirconium	2

These decontamination factors, with the exception of that for ruthenium, are the ratios of the fission-product concentrations in the salt bath to those in the final uranium monocarbide product. Since significant ruthenium removal occurs at the anode, the over-all value is given.

The third process for uranium carbide fuels[39–41] involves conversion of the fuel to uranium nitride and carbon by the action of nitrogen at 900°C. The uranium carbide is regenerated by heating to 1500°C *in vacuo* to reverse the reaction. Three cycles of this type have been completed on a sample of uranium carbide. Contrary to earlier preliminary results the uranium nitride was not pyrophoric, and no difficulty was encountered in repeating the cycle.

The rate of nitridation depends markedly upon prior exposure of the uranium carbide to water vapor, an effect noted previously in the oxidation reaction. Table III-5 shows nitridation rates of uranium monocarbide as a function of "age," which is a term referring to the time since arc melting that the sample was exposed

to air saturated with moisture at room temperature. In spite of its large influence on the reactivity of the carbide this type of exposure causes no noticeable change in its appearance.

Table III-5 EFFECT OF AGE ON REACTION RATES OF URANIUM MONOCARBIDE WITH NITROGEN[40]

(Temp., 800°C; Nitrogen Pressure, 360 mm; UC Composition, 4.55 Wt.% Carbon; and Particle Size of UC, −8 +16 Mesh)

Carbide age,* days	Cumulative weight gain,† mg/g		
	30 min	60 min	300 min
0	4.1	5.4	13.3
3	9.0	12.6	28.6
7	16.4	23.1	46.4
14	20.2	29.6	55.9
40	35.5	49.1	74.7
60	41.6	53.7	76.9

*Time of exposure to moisture-saturated air at room temperature since arc melting.

†Theoretical weight gain for complete conversion of UC to U_2N_3 is 84.3 mg/g.

Thermobalance studies indicate the order of the reaction to be 1.75, which corresponds to the rate equation

$$\frac{1}{(1-x)^{0.75}} = kt$$

where x is the fraction of carbide that has been nitrided at time t. The initial reaction rate is proportional to the square root of the nitrogen pressure, but the rate constant varies as the 0.825 power of the pressure, suggesting a complex rate-controlling mechanism. The initial rate also varies with the carbon content of the uranium carbide with a minimum at about 4.66 wt.% carbon.

Information has also been reported[39–41] on the reactions of uranium monocarbide with water vapor and with carbon dioxide. With water vapor a partial reaction increases the pyrophoricity of the carbide, and, again, "aging" increases its reactivity. A sample of reactive uranium carbide at 450°C in 20 mm of water-vapor pressure showed an initial weight gain of 2.0 mg/(min)(g). For the reaction with carbon dioxide, the initial rates at 400 mm of pressure were as follows:

Temp., °C	Weight gain, mg/(min)(g)
400	0.27
450	0.46
500	0.76
550	1.26
600	1.47
650	2.64

Variation of the carbon dioxide pressure at 450°C resulted in the following data:

CO_2 pressure, mm	Weight gain, mg/(min)(g)
50	0.11
100	0.27
200	0.41
400	0.46
600	0.55

In a flowing stream of carbon dioxide at 525°C, ignition of reactive uranium carbide was observed, and the sample was completely pulverized. The oxidation of uranium monocarbide by carbon dioxide is of considerable process interest since the reaction evolves less than one-third of the heat produced by the reaction with oxygen.

Miscellaneous

Studies of uranium tetrachloride absorption spectra from 300 to 2600 mμ at temperatures up to 850°C have been made in a variety of molten chloride systems.[44] Hexachlorouranate (UCl_6^{2-}) in equilibrium with at least one other species was indicated in all solvents except zinc chloride. The order of stability of hexachlorouranate ion in the various solvents was $CsCl\text{-}AlCl_3 = KCl\text{-}AlCl_3 > CsCl > KCl > NaCl > ZnCl_2$. Absorption spectra of rare-earth fluorides in molten lithium chloride–potassium chloride eutectic at 400°C have also been published.[45] French work has been reported in which the uranium species at various oxidation states in the same eutectic system were studied.[46] Cooling-curve analyses for the systems plutonium trichloride–rubidium chloride and plutonium trichloride–cesium chloride by workers at Los Alamos[47] indicate the existence of three double salts and two double salts, respectively. A point that may be of process

interest is covered in a report that describes the effect of radioactivity on the sublimation rate of molybdenum trioxide.[48]

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Section

IV

Reactor Fuel Processing

Waste Disposal

Hazards Evaluation of Tank Storage

A previous Oak Ridge National Laboratory (ORNL) study of the hazards of storing high-activity wastes in steel-lined concrete tanks showed that the apparent safety could be misleading.[1] The limited lifetime of the tanks plus the large volume of highly concentrated radionuclides could lead to a serious contamination hazard. Since the previous report a more thorough examination has been made of tank hazards, especially with respect to the manner and probability of tank failure.[2] The possibility of predicting the manner in which released wastes would be dispersed throughout the environment was also examined (on the surface, in the atmosphere, and in ground and surface waters). Reference 2 emphasizes methods of analysis that are applicable to any site. The various factors affecting tank hazards are discussed, and, where possible, typical calculations are given.

If the tank and cooling system maintain their integrity, there is no hazard; however, it is not expected that any tank will have a lifetime as long as the wastes that are contained therein. For instance, a 45,000-gal tank would still contain a total of 10^3 curies of activity after more than 10^6 years. In contrast, tank lifetime is assumed, in most studies, to be about 50 years.

Characteristics of the waste which tend to increase the probability of tank rupture are its corrosiveness, radiation field, and self-heating. The age of the nuclear industry has not been sufficient to develop accurate information on tank mortality. Data from experience at fuel-processing plants indicate that acid Purex wastes will corrode stainless-steel-lined tanks only about 1 mil per year. Corrosion by neutralized wastes would be expected to be much less. At this time, structural weakening by the radiation field eludes prediction. Only self-heating is immediately amenable to analysis.

To illustrate the calculation of temperature rise due to self-heating, assume that a 45,000-gal tank receives the high-activity wastes from the nuclear industry that are predicted for 1970. The tank is assumed to be spherical, to have a uniform temperature inside, and to be embedded in an infinite conducting medium that has thermal properties which are the same as those of the average of the earth's crust. The waste is presumed to be cooled until, at some time after filling, the cooling system breaks down or is deliberately shut down. The temperature will then rise. Figure IV-1 shows the length of time required for the waste to boil as a function of the age of the waste and the difference between initial temperature and boiling point.

It is apparent that the most danger of boiling occurs in the first several hundred years of storage. For instance, if wastes are initially at 20°C and the cooling system breaks down in 50 years, the contents will boil in 2.4 days, a relatively short time in which to correct the situation. Also shown in Fig. IV-1 is the length of time the wastes must be cooled to prevent boiling. This cooling time is such that if the cooling system is turned off permanently the steady-state temperature rise will just barely reach the boiling point.

It has been implicitly assumed throughout this discussion that, in the event of boiling, the tank will be forced to rupture. The probability of tank rupture due to boiling decreases with the increasing age of the waste. Counteracting this trend is the increasing decrepitude of the tanks with age. In addition to the weakening due to corrosion and radiation field, the tank will become weakened by settling, cracking, and

weathering, which are normal to concrete structures. Therefore it seems reasonable to expect the maximum probability of waste escape at some time toward the end of a tank lifetime and early in the life of the wastes.

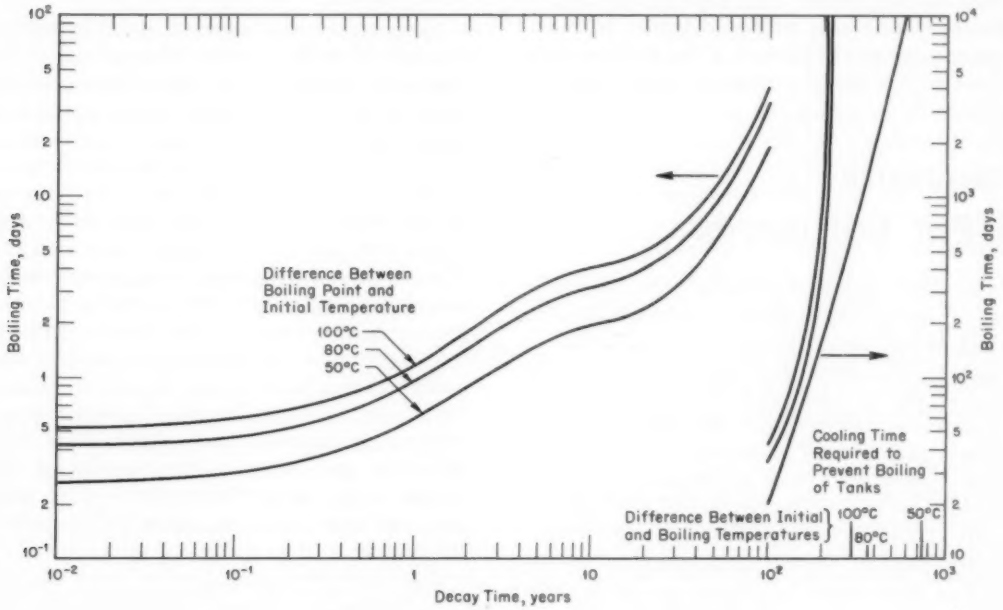

Fig. IV-1 Time required for waste to boil after cooling-system failure.[2]

Provision for off-gas and pressure-relief mechanisms will alleviate the danger of pressure rupturing the tank. However, if boiling occurs in the first 100 years, boiling of a full tank should be violent enough to force some of the liquid out of the tank.

There are other possibilities for release of the tank contents, most of them rather catastrophic (seismic disturbances, sabotage, physical shock due to explosions other than at the tank, or tidal waves near oceans). The probability of seismic rupture can be estimated from seismic tables for the given tank site; others present more difficulty. There probably would be no small leaks due to this last group of causes; any disturbances that would be large enough to break the tank walls would release a large fraction of the contents.

Upon rupture of the storage tank, the released waste can be dispersed into the atmosphere, into the ground (thence into ground and surface waters), or, by a relatively direct route, into surface water. Atmospheric contamination represents the case of most rapid contact with the population and the most rapid diminution of hazard. Spillage into the ground can form an external hazard if, by capillary action or other mechanism, the wastes reach the surface of the soil. Such wastes will, to some extent, be sorbed by soil and will be diluted by ground waters. Surface-water contamination is a direct hazard via drinking water; it is also an indirect hazard due to inclusion of the radionuclides in aquatic food chains.

The problem of atmospheric dispersion has received further consideration. The rate of contaminant release was estimated for the case where the waste was being vaporized by its own heat, and the vapor was not recondensed by the tank soil-cover. Assuming again the 45,000-gal tank with its radionuclides (2.9×10^8 curies of fission products) and allowing the tank contents to boil for 40 years after filling (a total heat power 1.83×10^5 cal/sec), the rate of release was calculated to be 3×10^2 curies of fission products per second. From previously calculated meteorological information on atmospheric dis-

persion of contamination, the air contamination at 28 km downwind, under adiabatic conditions, will be at its maximum at about 1.1×10^5 MPC (maximum permissible concentration). This number is expected to be an overestimate. The assumption of no condensation on the way to the surface is improbable. Also expected is a large, rapid fallout of the activity onto the surface. Prediction of the magnitude of these two events has not been attempted because of their lack of definition.

Economics of Pot Calcination

In an ORNL study to evaluate, from the standpoint of economics and hazards, the various steps leading to and including the permanent disposal of highly radioactive liquid and solid wastes, the costs of pot calcination of Purex and Thorex wastes were calculated.[3-6] The assumption was that the wastes were produced by a plant processing 1500 metric tons of uranium converter fuel per year at a burnup of 10,000 Mwd/metric ton and 270 metric tons of thorium converter fuel per year at burnup of 20,000 Mwd/metric ton. The costs were calculated for processing Purex waste in acidic and reacidified forms and for processing Thorex wastes in acidic and reacidified forms and with constituents added for producing an acidic Thorex glass. The costs were based on wastes that were assumed to be decayed for 120 days and for 1, 3, 10, and 30 years after reactor discharge prior to calcination.

The assumed processing cycle consisted of three periods: (1) the solids deposition period, during which liquid waste was pumped into the vessel at a sufficient rate to maintain a constant liquid level near the top of the vessel and the walls were held at 900°C so that the vessel filled with solids by evaporation; (2) the calcination period, during which the solid was heated to 900°C to drive off volatile constituents; and (3) change-out time, during which feed and off-gas lines were detached from a filled and calcined vessel, a storage fitting was welded on the top, the filled vessel was replaced by an empty one, and feed and off-gas lines were attached. In this assumed system, melting occurred during the calcination period with reacidified wastes due to the low melting point of Na_2SO_4 (884°C); therefore, following the calcination period, only about the lower half of the vessel was occupied. (It might be desirable with a reacidified waste to allow the melt to freeze after calcination and repeat the solids-deposition and calcination parts of the cycle to improve utilization of space in the vessel.)

Costs were estimated[5] for the assumed calcination-plant building as a function of cell-block size (which varies with different combinations of acid and alkaline wastes and with different calcination-vessel sizes) and as a function of shielding-wall thickness (which varies according to length of interim liquid storage). These building costs were amortized over 50 years at 4 per cent interest. Costs for the assumed process equipment were broken down into two categories and amortized over periods of 20 and 10 years. Building costs ranged from about $1.5 million to $4 million, resulting in annual costs which ranged from $70,000 to $185,000. Total capital costs per year, including process equipment, ranged from about $150,000 to $375,000 per year. Yearly operating costs ranged from about $600,000 to $1.4 million (40 to 90 man-years/year plus maintenance and overhead).

Calcination pots (right-circular cylinders) were assumed to be 10 ft in length and 6, 12, or 24 in. in diameter. About seven years of interim liquid storage would be required before acidic Purex wastes could be processed in 24-in.-diameter vessels. The number of pots required per year ranged from a minimum of 145 24-in.-diameter pots to a maximum of 9660 6-in.-diameter pots.

The total yearly cost (capital, operating, and pots) for operating the assumed calcination plant was evaluated for each of 12 waste combinations with up to nine combinations of pot diameter (a total of 90 combinations) for interim liquid storage periods of 0 to 30 years. These costs ranged from $3.1 million per year (using 24-in.-diameter pots) to $6.6 million per year (using 6-in.-diameter pots), depending on waste and pot-size combinations chosen, for 120-day-cooled wastes (no interim liquid storage) and from $1.1 million to $6.6 million per year for 30-year-cooled wastes. The corresponding ranges per unit of electric power would be 0.024 to 0.05 mill/kw(e)-hr for 120-day-cooled wastes and 0.0087 to 0.05 mill/kw(e)-hr for 30-year-cooled wastes.

Conversion of High-Level-Activity Wastes to Solids

Pot Calcination

At ORNL the pot-calcination process for converting high-level-activity wastes to solids is being studied on both a laboratory and an egnineering scale to provide design information for construction of a pilot plant.[3,7,8] Development work has been done with synthetic Purex, Darex, and TBP-25 wastes that contained millicurie amounts of ruthenium but has not been demonstrated on actual high-level-activity wastes.

The waste oxides that resulted from calcination of simulated TBP-25 wastes are being incorporated into glassy materials at elevated temperatures with various fluxing agents (borate, phosphate, and lead oxide).[7,8] Borate, which was added as tetraborate ($B_4O_7^{2-}$), tends to lower the softening point and viscosity of melts; however, it tends to cause foaming before the solids soften. Phosphate was added as the acid phosphate or hypophosphite ($H_2PO_2^-$), the latter serving as a source of phosphate as well as a reducing agent to control ruthenium volatility.[7] Lead oxide did not lower the viscosity and softening point of melts as well as borate. A big advantage of lead oxide over borate is that it does not cause foaming of the mixture prior to melting. Another advantage of lead oxide is that it yields higher density melts for the weight of additives required than other chemicals studied. This also implies greater volume reductions.[8] With the addition of mixed phosphate and borate fluxing agents, melts formed at 850 to 950°C were glassy solids when cooled and had densities of about 2.5 g/ml. Waste-volume reduction factors[7] were from 7.6 to 9.3. With the addition of mixed phosphate and lead oxide fluxing agents,[8] the melts formed at 900 to 975°C, had densities of about 2.8 g/ml, and represented waste-volume reductions of about 8.4.

The use of phosphite or hypophosphite to control ruthenium volatility is particularly attractive since these compounds are oxidized to phosphate (a fluxing agent).[7,8] The condensate from batch evaporation of Purex waste made 1.5*M* in sodium hypophosphite contained 5.4 per cent of the original ruthenium, whereas the condensate from a similar evaporation of waste made 1.5*M* in monobasic sodium phosphate contained 15.1 per cent. The condensate from semicontinuous evaporation of simulated Purex waste made 0.8*M* in phosphite contained 1.3 per cent of the ruthenium present. Nitric oxide is the principal gaseous product from the reaction between nitric acid and phosphorous acid and between iron or aluminum nitrate and phosphorous acid.[8] The best catalysts found for the reaction between nitrate and phosphite ions were silver, mercuric, and palladium ions.

Perona at ORNL has examined the effects of internal heat generation on the average processing rate in pot calcinations.[9] A sample calculation for Purex waste showed that a moderate heat generation rate of 5000 Btu/(hr)(cu ft) would decrease the time to fill a 12-in.-diameter calcination vessel from 78 to 55 hr. For the calcination stage of the process, in which the deposited solids are heated in the absence of a liquid phase, this same Purex waste would be calcined in less than 15 min, compared to about 8 hr in experiments with simulated wastes.

At Hanford, batch- or pot-calcination studies with simulated Purex high-level acidic waste solutions were continued.[3,10] Solution foaming during the boildown step, internal pressurization during the calcination step, and the weight of the calcines produced were investigated in simple and annular cylindrical pots which ranged in size from 3 in. in diameter and 7 in. high to 8 in. in diameter and 5½ ft high.[10]

A series of runs was made to determine qualitatively the factors affecting foaming. In addition to the boilup rate, solution foaming was found to be dependent on the pot geometry and on the waste composition. The majority of the waste-solution compositions were within the range which produces a calcine that becomes molten at less than 900°C. Neither silicone antifoam agents nor air sparge were able to control the foam from a waste solution that contained both phosphate and borate.

Severe corrosion of the type 304L stainless-steel calcination pot occurred during the boildown step with solutions that contained phosphate and borate. In places, penetration of the ¼-in.-thick wall was as high as 60 per cent. Boric acid was observed to steam distill from the solution and condense on surfaces above the pot.

Internal pressures can develop within the solids during the calcination step when only partial melting occurs and when the sulfate is in

excess of the stoichiometric sodium equivalent. A maximum internal pressure of 0.6 psi was measured in a 3-in.-diameter by 7-in.-high pot during the calcination step with a waste composition known to produce internal pressurization. No internal pressurization was apparent in a run made in a 6-in.-diameter annular pot with the same waste solution. The generation of internal pressures in a large-diameter pot is considered less likely to occur because of the greater probability of cracks or fissures developing in the upper layer of calcine through which the decomposition gases can escape.

Spray Calcination

Hanford has continued its study of combining the radiant-heat spray-calcination and the pot-calcination processes.[3,11] The laboratory-size spray calciner was modified for testing as a spray preconcentrator.[11] A preconcentrator would greatly reduce the heat duty of a batch calciner since the evaporation of water constitutes the major portion of that heat duty. The advantage of a spray preconcentrator for this service is that no fouling of heat-transfer surfaces will occur because the feed droplets will not contact any heated surfaces. A demonstration test indicated the feasibility of using a spray unit as a preconcentrator for high-solids-content feed streams. Volume reduction as high as 50 per cent was obtained, and several concentrate samples crystallized upon cooling. Entrainment losses to the condensate were less than 0.1 per cent.

Hanford has briefly tested a Mallinckrodt flame denitrator to determine the potential of this technique for waste fixation.[11] The Mallinckrodt pilot-plant unit shown in Fig. IV-2 was modified and was used for this waste-denitration work. The simulated waste-feed solution was sprayed down through the reactor. An annular propane-air burner surrounded the spray nozzle, and the cocurrent combustion gases provided the drying-calcining temperatures.

Although some difficulties were encountered, in comparison with the radiant-heat calciner the flame denitrator appears to have the following advantages: (1) a choice of a wider range of construction materials by eliminating heat transfer through the reactor walls; (2) a simpler source of heat, particularly for pilot-plant studies; and (3) a possibly higher capacity. The disadvantages include (1) a considerably higher off-gas volume even with oxygen in place of air in the fuel stream; (2) a relatively narrow zone of satisfactory operating conditions between stable flame temperatures and the temperature at which waste solids melt; and (3) the difficulty of instrumenting the reactor to indicate off-stand and operating conditions.

The product from the flame denitrator resembled that from the radiant-heat spray calciner. Bulk density of the product was low, and the angle of repose was about 70°. As in the radiant-heat spray calciner, reducing atmospheres, attained in the flame denitrator with excess propane, appeared to improve the quality of the product.

Fluid-Bed Calcination

At the Idaho Chemical Processing Plant (ICPP), laboratory- and pilot-plant studies on the fluid-bed calcination technique for reduction of aqueous aluminum nitrate waste solutions to solid alumina form have continued.[3,12,13] The pilot-plant 2-ft-square calciner was operated to study the performance of individual feed spray nozzles designed for use in the Demonstrational Waste Calcining Facility in an effort to select a design that offers maximum resistance to erosion in combination with reasonable control of the calciner operation.[12,13] Flat-faced nozzles that were originally provided gave good operating control (presumably related to the spray pattern) but exhibited prohibitive erosion rates. An extended convergent cone tip has shown excellent erosion resistance but a relatively narrow operating range with respect to air-liquid ratios; an extended divergent cone tip proved inoperable in continuous runs, at any air-liquid ratio attainable in the test equipment, due to uncontrollable particle growth which interfered with heat transfer.[12] Excessive feed-nozzle-tip erosion rates were experienced with hardened stainless steel and alumina-coated titanium flat-faced nozzle tips.[13]

In other runs in the 2-ft-square calciner, data were obtained on (1) the calcine particle porosity as affected by temperature and feed concentration, (2) the alpha alumina content as a function of temperature and nozzle air rate, and (3) the effect of the starting bed material (sand) on the evaluation of plant operating variables.[12,13] The intraparticle porosity of the alumina generated is primarily governed by the

concentration of the aluminum nitrate in the feed and the bed temperature; the more desirable low-porosity (high density) alumina is produced at lower temperatures (400°C as compared with 500°C) by use of a low-concentration (1.5*M*) feed. The formation of alpha alumina was found to be related to calcining temperature and nozzle air-to-liquid volume ratio (NAR) in runs carried out during this period; a low temperature (400°C) and a reduced NAR resulted in minimum alpha alumina formation. An increase in either factor resulted in an increase in alpha alumina production which was reversible by again lowering the factor under investigation. Sand, in place of previously calcined alumina, was used successfully as a starter bed and

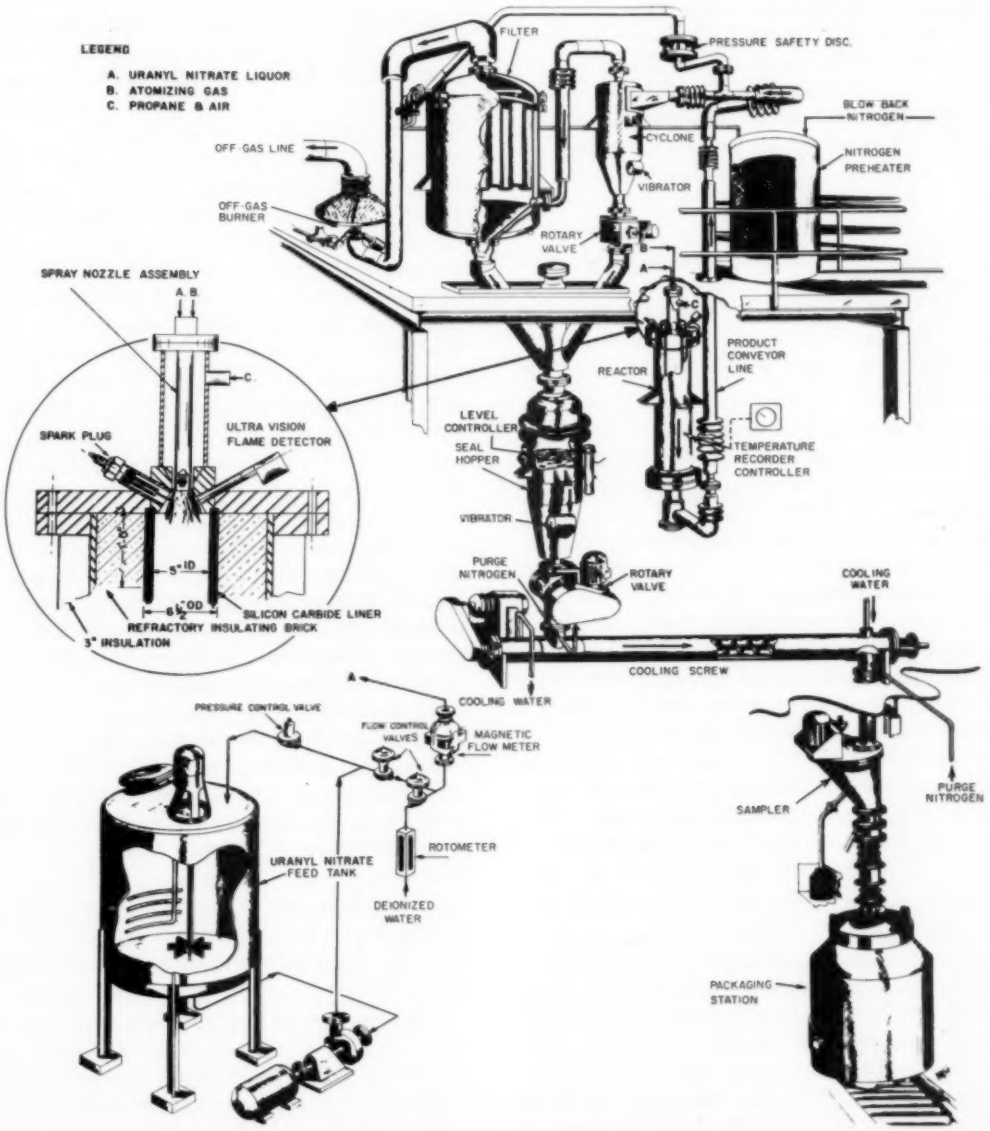

Fig. IV-2 Flame denitration pilot plant.[11]

offered the advantage of being able to assess rapidly (within 24 hr) the characteristics of the newly formed alumina without having to wait for essentially complete bed replacement (50 to 100 hr).[13]

Laboratory exploration of the calcined alumina system has demonstrated that a combination of the presence of sodium nitrate and an atmosphere which contains air, water vapor, and oxides of nitrogen markedly increases the rate of formation of alpha alumina from amorphous alumina in the 400 to 600°C range, but the kinetics and mechanisms of the reaction remain to be determined.[12] Quantitative assignment of the effect of sodium has not been possible since it is apparently interrrelated with other undefined factors involved in the previous calcination history.[13] Exposure of samples of alumina from the pilot-plant calciner to the electron beam in an electron microscope caused apparent changes in crystal structure (as indicated by sharpening of rings in diffraction patterns) within a few minutes.[12] More recent investigation has indicated that this effect, if real, is not caused by radiation.

In the first integrated test of the Demonstrational Waste Calcining Facility, control of the calciner-bed temperature at 400°C appeared to be adequate with a liquid feed rate of 60 gal/hr and a superficial fluidizing velocity of 1 ft/sec; the NaK pump was operated at 68 per cent of capacity under these conditions.[13]

Laboratory studies were continued to determine the optimum calcination temperature of acid waste solutions that are typical of those obtained from hydrofluoric acid dissolution of zirconium-based fuel.[12] These waste solutions contain, as major chemical components, zirconium, aluminum, fluoride, and nitrate. The proposed method involves precipitation of the zirconium, the fluoride, and much of the aluminum by the addition of calcium oxide and calcination of the resulting slurry.

Calcination at 400, 435, 465, 500, and 535°C indicated that no detectable amount (less than 0.25 per cent) of the total fluoride was volatilized and collected in the caustic scrubbers. The leachability of the residue in water at 25°C decreased from 11 to 2 per cent over the temperature range. The ratio of calcium to fluoride in the leachate also decreased with increasing temperature, suggesting that, at the higher temperatures, the soluble material was largely calcium fluoride; whereas at the lower temperatures there was also some unreacted calcium oxide which dissolved. These results give promise that utilization of the stainless-steel Demonstrational Waste Calcining Facility for the treatment of zirconium fuel-processing wastes would be feasible.

Conversion to Glasses

In the Brookhaven National Laboratory (BNL) study of ultimate disposal of high-level wastes, major emphasis is being placed on the formation of phosphate glasses as a means of incorporating the fission products in stable media.[14–17] Construction of the small pilot plant (Fig. IV-3) that will produce phosphate glass from simulated Purex waste was essentially complete,[17] and operation was expected to begin early in December 1961. Initially the plant will be operated on a semicontinuous basis. This plant will permit study of construction materials and glass-handling techniques on a scale approaching a practical one. It is designed to have a capacity of 1 cu ft of glass product per 24 hr which, with a volume reduction factor of 110 to 120, would correspond to a volume of unconcentrated Purex waste from the processing of 1 ton of uranium.

Two processes will be studied: (1) the semicontinuous and (2) the fully continuous. In the semicontinuous process the molten glass will be formed directly in individual final storage containers. In the fully continuous process the glass will be formed in a central crucible and fed to separate storage containers. The essential difference lies in the type of high-temperature crucible since the denitration step and the collection and absorption of off-gases are carried out with the same equipment in both processes.[15] In the semicontinuous process a Coors Porcelain Company alumina crucible that is 3 in. in outside diameter by $6\frac{1}{2}$ ft in length will be used.[16,17] This crucible will be filled to contain approximately $1\frac{1}{2}$ cu ft of molten glass, after which the crucible and contents will be cooled, removed from the furnace, and sent to final storage.[16]

The crucible for the fully continuous operation will be a vessel of much smaller capacity (8 in. in outside diameter by 12 in. in length), but it is expected to operate with about the same daily throughput as the crucible in the semicontinuous operation.[16,17] The glass that forms in the crucible will be withdrawn through a bottom

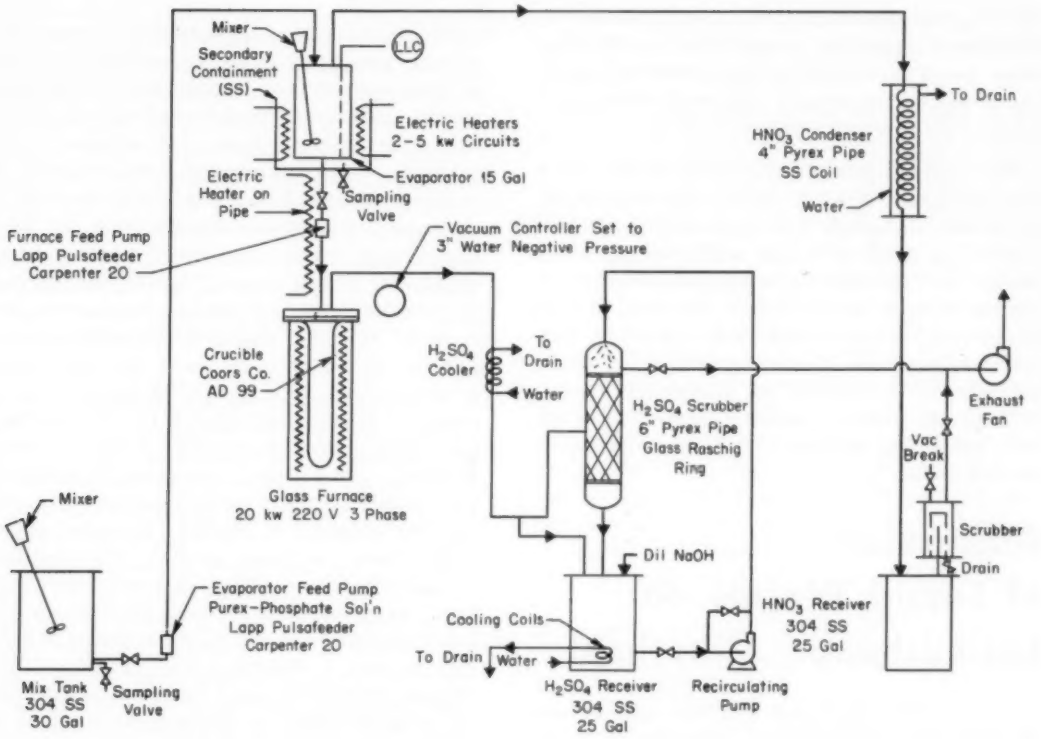

Fig. IV-3 Flow diagram of BNL Purex phosphate-glass pilot plant.[17]

outlet which is fitted with a freeze valve. The crucible will be patterned after the platinum-clad molybdenum crucibles used throughout the glass industry to make high-purity optical glass. The high cost of platinum does not rule out its use as a practical crucible material for the formation of phosphate glass from Purex wastes. A platinum-clad Inconel crucible is being considered.[17] Nonporous, high-strength alumina crucibles encased in prestressed metal (jackets) are also being studied and offer considerable promise.

The results of screening tests showed that Coors AD99, a high-density "zero-porosity" alumina, and platinum show no corrosion or deterioration[15] after contact with the molten glass for 14 days at 1100°C. The platinum testing program was expanded to include test specimens of platinum alloys that contained rhodium, iridium, or gold. These were examined after exposure to molten Purex-phosphate glass[17] at 1100°C for 744 hr. The rhodium-containing material showed some porosity on microscopic examination, but all other specimens appeared to be undamaged. Moreover, apparently no damage occurred at the air-glass interface. It is important to note that, although the specimens were exposed only to the molten phosphate glass at temperatures as high as 1100°C, the crucible would be exposed to decomposing sulfates as well. For the low-temperature vessel in which the evaporation occurs, Carpenter 20 and Nionel appear to be most promising as construction materials.[15]

Hanford has been investigating the incorporation of strontium and cesium into glass or glass-ceramic systems that could serve as heat or radiation sources as well as final or temporary storage forms.[18] Tests were made on 16 compositions that contained 29 to 59 per cent strontium and four that contained 50 to 59 per cent cesium. The most promising strontium-containing composition is a phosphate glass that contains 49 per cent strontium. It devitrifies rapidly during cooling and therefore cannot be classified as a

"good" glass. However, it can be cast at 1350°C and has a solubility, when boiled in distilled water for 4 hr, of approximately 0.04 per cent. The other compositions that were tested had solubilities 10 times greater or more.

The cesium glasses that were tested were also phosphate glasses, being single mixtures of cerium phosphate and aluminum phosphate. They were found to be too water soluble to be attractive. The more resistant lost about 22 per cent in 4 hr in boiling water and were almost completely disintegrated. The solubility was much reduced by the incorporation of small amounts of zirconium or lanthanum oxides. Attempts to prepare silicate glasses were not very promising because of the high volatility of cesium oxide.

Adsorption of Liquid Wastes on Ion-Exchange Materials

In laboratory studies at Hanford, applications of adsorption and mineral reactions to waste fixation and containment were further investigated.[3,19] In the Micro Pilot Plant, steam stripping was demonstrated to be effective for removing ammonia and organics from actual Purex tank-farm condensate wastes. These impurities, although present in low concentrations, chemically interfere with ion-exchange reactions and physically foul the beds. The stripper[19] reduced the ammonia from 130 to 5 ppm, the butyl phosphates from 150 to 1 ppm, and the hydrocarbons from 35 to 4 ppm.

The only radioisotopes detected in the overhead distillate were iodine ($\sim 1 \times 10^{-5}$ μc/ml) and ruthenium ($\sim 3 \times 10^{-6}$ μc/ml). Most of the ruthenium, as well as the radioisotopes of strontium, cerium, zirconium, niobium, and cesium, remained in the stripper bottom stream. To reduce the residual organic impurities, this stream was passed through activated carbon. The carbon effluent was then passed through a cation exchanger (Amberlite IR-120 in the hydrogen form) which reduced the concentration of all the radioisotopes present except ruthenium to less than 10 per cent of their MPC_w (maximum permissible concentration in water) for 5000 column volumes.

The selectivity of clinoptilolite for adsorbing cesium was found to be permanently increased by heat-treatment.[19] Heating for 2 hr at 400°C nearly doubles the capacity of the mineral for adsorbing cesium from 1*M* sodium nitrate solution. Higher treatment temperatures decreased the equilibrium coefficient markedly.

Hanford laboratory experiments in which neutralized Purex high-level and aluminum decladding wastes were passed through columns of phenolic resin indicated a cesium adsorption capacity (to 50 per cent breakthrough) equivalent to about 30 bed volumes and to 200 bed volumes of the wastes, respectively.[19] Since the principal chemical difference between the two wastes is the excess caustic present in the decladding solution, equilibrium experiments confirmed that, with increasing concentrations of hydroxyl ion, the sorption of cesium increased significantly over the range studied. With a column of phenolic resin which utilized Purex high-level-waste supernatant solution that contained 2.8*M* hydroxyl ion and which operated at a flow rate to give a residence time of nearly 2 hr, a cesium decontamination factor of greater than 10^4 was obtained on the equivalent of 40 bed volumes of waste; a 50 per cent breakthrough did not occur until about 150 bed volumes were passed. The elution of cesium from phenolic resin can be accomplished with acids, sulfuric acid being the most promising because nitric acid attacks the resin and hydrochloric acid corrodes most equipment materials.

Honstead and associates[20] at Hanford have reviewed the mineral reactions used (and their application) to decontaminate radioactive wastes. Two general types of reactions are discussed: (1) mineral replacement and (2) adsorption. The mineral replacement type covers reactions between a mineral and a constituent of the waste resulting in the formation of a new crystal lattice and the inclusion of radioisotopes in the final product. The adsorption type covers reactions with mineral surfaces, including ion-exchange and specific adsorption processes.

Reisenauer and Ames[21,22] have summarized a preliminary Hanford study on the adsorption on Florida pebble phosphate of plutonium from an acidic waste (*p*H 2.1 to 2.8). Adsorption of plutonium from these wastes was found to occur over a range of plutonium concentrations from 0.4 to 4.7 mg/liter. Prompt elution (with 1*M*

sodium carbonate) recovered at least 90 per cent of the plutonium within 2.8 column volumes, but elutions not effected promptly removed as little as 10 per cent of the plutonium. Regeneration with solutions of phosphate ion restores the apatite surface and actually increases the effective adsorption capabilities for plutonium. Some of the advantages of the mineral-bed process would be radiation stability, chemical stability above *p*H 2, elution with nonhazardous chemicals, and small elution volumes. A disadvantage is the incomplete product recovery except when promptly eluted.

Fundamental studies have been carried on at ORNL on the reactions of Sr^{90} with minerals.[3,23,24] In characterizing the reactions of strontium with sorbent materials, four possible mechanisms are suggested: (1) ion exchange as an absorption process exemplified by the resins, clinoptilolite, and the clay minerals; (2) ion exchange as an adsorption process characterized by the reaction of alumina; (3) metasomatic replacement as characterized by the calcium carbonate-phosphate reactions; and (4) precipitation reactions as evidenced by natural vermiculites and clinoptilolite in contact with phosphated waste.[23]

Selected ion-exchange materials that were tested are shown in Table IV-1. In general, the higher the exchange capacity, the higher the removal of strontium. The data for natural materials (biotite and vermiculite) that have been treated to increase the exchange capacity by removal of lattice potassium by the sodium tetraphenylboron treatment emphasize the importance of the cation-exchange capacity for strontium sorption.

Earlier data have shown much promise for alumina in the removal of strontium from simulated waste solutions. Several other oxides (lead, iron, and cerium) were tested, and cerium dioxide showed similar behavior. These materials were found to have very low ion-exchange capacities; alumina, for example, showed less than 1 meq/100 g. Although the cause of the selectivity for strontium is not known, it is thought that the amphoteric qualities of alumina and cerium dioxide are responsible. The results of tests of the influence of *p*H on the performance of alumina and cerium idoxide have shown that the alumina response is greatly influenced by *p*H. A significant difference has been indicated between alumina and vermiculite for the removal of strontium. Evidence accumulated thus far suggests that alumina removes by a surface reaction and that vermiculite removes by absorption. Thus surface-reactive materials such as alumina may be useful in removing traces of strontium from wastes.

Results are shown in Table IV-2 for several materials that were tested when phosphate was added to the waste. The reaction that removes strontium was reported to be a metasomatic replacement reaction. The beneficial influence of phosphate on the removal of strontium by natural vermiculite is caused by the formation of magnesium phosphate precipitate; the magnesium is present as an exchangeable ion on the

Table IV-1 REMOVAL OF STRONTIUM FROM SIMULATED WASTES BY SELECTED ION-EXCHANGE MATERIALS[23]

Material	Ion-exchange capacity, meq/100 g	*p*H	Per cent of strontium removed			
			1-hr contact	4-hr contact	24-hr contact	72-hr contact
Dowex 50W-X12	500	5.2	50	74	93	98
Duolite C-3	250	3.0	29	52	85	91
Kaolinite	13	7.5	12	11	12	14
Nontronite	98	7.0		19	48	53
Vermiculite	67	7.5	11	16	31	36
Montmorillonite	91	8.4	35	44	44	44
Clinoptilolite	200	7.0		35	75	90
		8.5		44	78	91
2 × Na-tetraphenylboron vermiculite	140	8.5	38	51	75	80
2 × Na-tetraphenylboron biotite	97	8.5	38	53	69	67
Biotite	4	8.5	2.2	2.3	3.4	2.3

natural material. When sodium ions are substituted for magnesium on the exchange site, vermiculite no longer shows any benefit from the addition of phosphate. These tests in Table IV-2 also show the superiority of calcium phosphates for the removal of strontium. In soils where most of the saturating cations are calcium, the influence of phosphate will be an important consideration.

The influence of phosphate on the removal of strontium by clinoptilolite was investigated. Since the material contains calcite impurities, it was suggested that the metasomatic replacement reaction was responsible for the removal. It is apparent from the data given in Table IV-2 that the addition of phosphate ions is beneficial to the natural clinoptilolite system. With as low as 100 ppm phosphate at *p*H 10.5, removal was improved.

A comparison of strontium removal[24] by sodium-vermiculite, clinoptilolite, Duolite C-3, and Dowex 50 showed that sodium-vermiculite is ineffective at low *p*H but competitive at basic *p*H's. At low *p*H, vermiculite decomposed. The other alumino-silicate (clinoptilolite) showed a slight decrease in strontium removal at *p*H 2, whereas the organic resins performed effectively in the entire *p*H range investigated.

Jacobs at ORNL has summarized work done on the removal of cesium with small columns of vermiculite.[25–27] Particle-diffusion processes were noted to have a pronounced influence on cesium breakthrough curves obtained from small columns that were operated for rather short periods of time. For full-scale-size columns, it may be necessary to correct for this phenomenon since the cesium loading increases with increased time of column operation. For prolonged times of column operation, the effects of particle diffusion are not so pronounced. The choice of particle size for an operating column may be determined, in part at least, by the kinetics of the exchange reaction. An understanding of the reaction mechanisms involved in the sorption of cesium by vermiculite has led to improvement of the cesium-sorptive properties in vermiculite columns, either by treatment of the vermiculite or by addition of potassium salts to the waste stream.

Table IV-2 THE EFFECT[23] OF ADDING SODIUM PHOSPHATE FOR REMOVAL OF STRONTIUM (*p*H = 9.0)

Material	Contact time, hr	Per cent of strontium removed at a phosphate concentration (ppm) of				
		0	100	500	1000	5000
$CaCO_3$*	1	1.3	0.3	1.2	3.2	5.2
	4	0.6	0.3	10	22	43
	24	0.0	1.6	76	91	99
	72	0.0	29	96	99	~100
Natural vermiculite*	1	9.6	6.8	7.4	13	13
	4	17	14	16	24	25
	24	31	32	29	35	55
	72	36	38	42	44	68
Sodium vermiculite*	1	15	15	12	11	7.4
	4	20	22	21	12	8.4
	24	40	41	38	42	22
	72	50	51	50	47	29
Alumina*	1	26	30	26	35	34
	4	32	44	44	55	47
	24	40	60	67	71	62
Clinoptilolite†	1	34	56	71	66	
	4	61	76	91	90	
	46	92	94	96	96	
	95	94	95	97	97	

*pH = 9.
†pH = 10.5.

The sorption of radionuclides by natural organic materials was studied at ORNL[28] and at Johns Hopkins University.[29] At ORNL the results from slurry studies showed that peat and lignite sorbed strontium and cobalt much more effectively than they did cesium. (With inorganic minerals, cesium was sorbed most effectively and strontium and cobalt were sorbed less efficiently.) Ruthenium removals were lower than those for strontium and cobalt; however, the removal of ruthenium was influenced least by stable-ion impurities (sodium and calcium). In column experiments, mixed-bed columns of peat and vermiculite, peat and lignite, and lignite and vermiculite were tested. The influent solution was composed of demineralized water that contained 1000 ppm sodium nitrate ($NaNO_3$) and 100 ppm calcium chloride ($CaCl_2$), spiked with approximately equal trace amounts of Cs^{137}, Sr^{85}, and Co^{60}. Initially the *p*H was 2.5, but, because activity started passing through the columns almost immediately, the *p*H was readjusted to *p*H 10. In these tests the lignite-vermiculite columns performed most effectively.

In the investigation at Johns Hopkins University, the retention of ruthenium and cesium in contact with soil and fermentable materials such as sawdust and peat was studied.[30] G. T. Bryant and associates obtained the following general conclusions using sodium nitrate solutions of $0.5M$ to $2M$ and digestion storage periods up to 120 days:

1. The retention of ruthenium on soil-sawdust mixtures increases with storage period for sodium nitrate concentrations up to $2.0M$.
2. Some increase in retention of ruthenium on soil-peat mixtures occurred, but the increases were not very pronounced.
3. There was no applicable increase in retention with time of cesium on soil-sawdust mixtures.
4. There was no increase in retention with time of cesium on soil-peat mixtures. The peat, however, showed a greater capacity for retaining cesium than the sawdust.

Final Disposal Methods

Disposal into Salt Formations

Laboratory and field studies conducted by ORNL have placed prime importance on the problems related to the direct disposal of high-level radioactive liquids in natural salt formation.[3,30] It is now apparent that high-level wastes will be converted to solids by the various calcination schemes in the next few years, and, further, that some safe ultimate disposal site for these solids must be developed. Because of its many advantages, salt is felt to be one of the most promising media for this disposal. As a result, primary emphasis has now been changed to studies relating directly to solids disposal or to studies that are applicable to disposal of both solids and liquids. Some of the items that are being studied as a part of the economic analysis of high-activity disposal in salt are (1) the storage of liquids in rooms with recessed floors, (2) the storage of pot-calcination vessels in racks above the floor, and (3) the storage of pot-calcination vessels in holes in the floor.[30–32] An important variable is the amount of mine space required for safe dissipation of fission-product heat.[32]

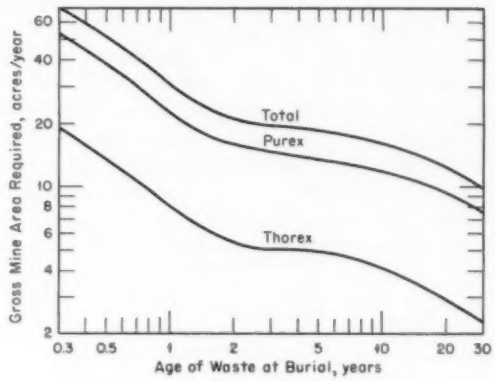

Fig. IV-4 Gross mine-area requirements for liquid-waste storage.[32] (Fifty per cent utilization of gross area for waste storage is assumed.)

For the disposal of liquid wastes in rooms with recessed floors filled with granular salt, calculations have been made of the total mine-space requirements for storing the output from processing an assumed 1500 tons of uranium per year and 270 tons of thorium converter fuel per year.[31] The gross mine area required, as a function of decay time before disposal, is shown in Fig. IV-4. For example, wastes aged two to ten years would require 21 to 16 acres per year. These curves assume that only 50 per cent of the gross mine area is used for actual waste storage but do not take any credit for lowering

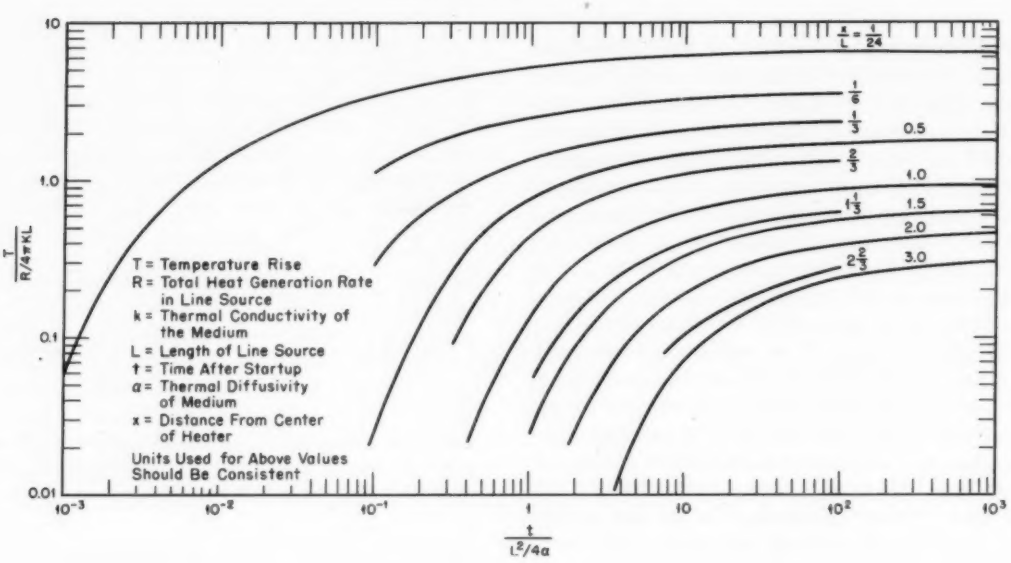

Fig. IV-5 Temperature rise around a line source with a constant heat-generation rate.[33]

the peak temperature rise because of less than 100 per cent utilization.

Since the cylinder is a likely storage container geometry for solid wastes, it is desirable to have a solution for temperature rises about cylindrical heat sources.[33,34] An equation for a line source of constant heat-generation rate has been developed. If the cylindrical source is long compared with its diameter, a good approximation is given of the temperature rises in the medium surrounding the cylinder (other equations are available for obtaining the temperature profile within the cylinder itself). The time-temperature profile on a line perpendicular to the center of the constant heat source at distances from the center of $\frac{1}{24}$, 0.5, 1.0, 1.5, 2.0, and 3.0 times the length of the source has been calculated. This profile, along with curves for additional values of x/L which were obtained from a cross-plot, are shown in Fig. IV-5. These curves show reasonable agreement with actual experimental measurements that were carried out in the Hutchinson mine.

A study conducted at the University of Texas has concluded that the storage of radioactive wastes in salt cavities is feasible.[35,36] This is the result of an investigation of the seepage of wastes out of salt formations and of the closure of cavities due to plastic flow of salt.[36] Both problems are considered to be negligible. Calculations have shown that wastes can be confined in salt beds for over 500 years, even if the formations had permeabilities of the same magnitude as the laboratory test results indicated. Such computations are considered extremely conservative since the permeability of undisturbed underground salt is much smaller than the values obtained in the laboratory tests. If the underground salt does have any permeability, the waste will become supersaturated as it passes outward from the cavity and will therefore cause recrystallization and precipitation of the salt. This in turn will block the pore passage and reduce the permeability to zero.

Disposal by Hydraulic Fracturing into Shale

ORNL is investigating the feasibility of disposing of liquid radioactive waste by mixing it with cement or some other hardening agent and then injecting it, while still fluid, deep into a bed of rock by pumping it down a specially constructed well.[37-40] The pressure that will develop at the bottom of the well will force the rock to fracture and separate, and the waste-cement mixture will then flow out into the rock in a thin sheet and harden. A preliminary field experiment was conducted[37] by pumping some

27,000 gal of cement grout into a local shale formation at a depth of 3000 ft.

A second experiment in hydraulic fracturing was carried out in two parts. The first batch consisted of a total volume of 91,567 gal of grout, which contained 222 tons of cement, 12,500 lb of bentonite, and 25 curies of Cs^{137}. This batch was injected into the shale at a depth of 934 ft. One week later a second batch of 132,770 gal, which contained 416 tons of cement, 17,000 lb of bentonite, 25 curies of Cs^{137}, and about 1 curie of Co^{60} was injected into the same well at a depth of 694 ft. The pressures required were somewhat higher than anticipated: 1700 to 2000 psig (surface) for a pumping rate of up to 150 gal/min for the first injection and 2000 to 2300 psig for a pumping rate of up to 300 gal/min for the second injection. These pressures are more than the static weight of the overburden, and, allowing for friction losses, it is probable that some force was required to bend or compress the overlying rock as well as to lift it. The pumping time for each injection was 11 hr, although each injection could have been made more rapidly.

Precise measurements of the elevations of a net of bench marks before and after each injection showed a clear pattern of uplift on each occasion of up to about $\frac{1}{8}$ in. and extended out after the first injection to distances of from 350 to 750 ft and after the second injection to distances of from about 700 to 1000 ft. Precise measurements were also made of the very slight tilting of the land during each of the injections.

Test wells were drilled in an effort to determine the extent, depth, and thickness of the two grout sheets. One point that has been clearly established is the poor correlation between the amount and extent of the observed vertical uplift of the land surface and the thickness and extent of the grout sheets. In several places cores of the upper grout sheet showed that it consisted of four sheets with a total thickness of $\frac{1}{2}$ in., whereas the surface uplift at these points measured only 0.1 in. or less. Under these circumstances the surface uplift is a poor guide to the location and extent of the grout sheet, and it is not possible to map the position and area underlaid by a grout sheet from surface measurements.

With this possible exception, the second fracturing experiment appears at this stage to have given results favorable to the possibility of actually disposing of radioactive waste at Oak Ridge by hydraulic fracturing.[38] It has shown that it is possible to inject into the shale, at depths up to at least 1000 ft, individual batches of liquid-cement mixtures of over 100,000 gal and that the fractures formed by the injection, even when located in relatively unfavorable local structures, extend outward laterally and show no inclination to break up toward the surface even when forced upward for short distances by sharp folds or faults.

Because the method shows such practical promise, three further lines of investigation have been initiated.[38] First, negotiations were completed with Westco Research, Fort Worth, Tex., to develop a waste-cement-clay mixture suitable for use in waste disposal by hydraulic fracturing, and the proposed subcontract was submitted to AEC for approval.[40] Second, a deep test well has been started at ORNL to core the rocks below the quartzite to a total depth of about 3000 ft to see if any of these deeper formations, which are not exposed at the surface, would be suitable for this method of waste disposal.[38] Rock that is well suited to disposal operations has been encountered[39] from 1500 ft to the present bottom of the hole (2200 ft). Third, ORNL has prepared a conceptual design of a possible waste-disposal plant to handle the current medium-level waste stream by hydraulic fracturing. The cost of the complete plant[38] has been estimated at $860,000.

ORNL is at present producing an average of 7000 gal of medium-level waste per day, which is to be reduced in volume (by evaporation) by a factor of 10. In two months this would result in some 42,000 gal of waste concentrate containing about 1800 to 2000 curies of activity. This waste concentrate, mixed with clay, cement, and possibly other additives, would make up a total volume of some 60,000 gal. This would be injected as a single sheet at the bottom of the disposal well and would then be plugged back upward a distance of about 10 ft with neat cement (cement mortar without sand). Two months later the next batch would be injected 10 ft above the first, and so on, until five years later 30 individual batches would have been injected at 10-ft intervals into the 300 ft of suitable shale. If the deep test hole shows additional suitable rock in depth, the life of the original disposal well can be correspondingly increased. When the first well must be abandoned, several more, drilled some 600 or 700 ft from the first, can each be

used in turn, and eventually the injection plant itself can be moved to a new location.

Initially the disposal cost will probably fall between $0.50 and $1.00 per gallon of waste concentrate; however, this will depend largely on operating, maintenance, and amortization costs which have not yet been determined. This is, however, except for monitoring, the total and final cost for permanent disposal. It should not be compared directly with such alternatives as tank storage or even conversion to a solid unless the cost of storing and monitoring the solid is also included.

Disposal into Porous Strata of Deep Wells

The disposal of radioactive waste solutions into deep permeable formations provides a means for isolating large volumes of low-activity waste from the circulating regimen of ground water, surface water, and atmospheric water.[41–43] In order to coordinate the efforts of various cooperating agencies involved in this program, the AEC's Reactor Development Division has named an *ad hoc* advisory committee on programs related to the injection of radioactive liquid wastes into deep permeable formations.[42,43] A group at the University of California has studied the theoretical and practical aspects of radionuclide dispersion in porous media under various operating conditions. A program at the U. S. Bureau of Mines has been primarily concerned with the physical aspects of injection as limited by the presence of suspended solids and flocs in the discharge solution or by chemical reactions in the receiving formation. At ORNL initial efforts will be directed primarily to a determination of the expected movement of the radionuclides in the disposal formation.[43] Some work is planned on the definition of the dispersion of solution fronts, but the primary effort will be concerned with the sorptive properties of cores that are obtained from typical permeable formations. Although simple models of ion exchange can be used for approximating the movement of specific radionuclides in a geologic formation, the effect of the formation on the chemistry of the percolating solution must be considered before a comprehensive picture can be developed.

Sea Disposal

Two reports have been issued which are related to ocean disposal;[44] these reports were prepared for the Commission by Advanced Systems Development Division, PneumoDynamics Corporation, El Segundo, Calif.[45–48]

The first report is concerned with the environmental surveys conducted at two deep-sea sites off the Pacific Coast which are designated by the Commission as areas where low-level radioactive wastes may be disposed of.[45,46] These surveys reveal that there is no detectable radioactivity attributable to waste-disposal operations at the two sites. The water depth at both sites is at least 1000 fathoms (6000 ft), the minimum depth at which AEC permits sea disposal. These sites have long been designated as explosive and chemical dumping grounds. Since 1946 some 14,000 curies of radioactive material in 22,000 packages have been disposed of at the Farallon Islands site. Disposal of radioactive material in the Santa Cruz Basin site began in 1953, and, at the time the survey was made, approximately 60 curies in 3000 packages had been disposed of there. In addition to the surveys of these two sites, similar studies were conducted at a third site, an area not used for disposal, for background comparisons.

The second report gives the results of an investigation of immersion effects on waste containers for ocean disposal.[47,48] As an added safety factor, the Commission has stressed the desirability of confining the low-level wastes until they reach at least the required 6000-ft level in the sea. One hundred and sixty-four containers were tested at sea in one of two ways: either by controlled lowering to 6000 ft and photographing them at 12-sec intervals on the way down or by uncontrolled lowering of the containers and tracing their descent by means of a depth-sounding device. Both methods were used simultaneously whenever possible. Most of the containers tested at sea were actual packages used by Commission contractors and licensees. They were selected at random from all the operating sea disposers of the United States, varying in types from 30-gal steel drums to concrete blocks weighing as much as 15 tons.

One hundred and twenty-three of the 164 containers involved in the test program were successfully photographed.[47] Most of the 164 containers were traced with the depth sounder to the sea floor. Structural changes were evident in varying degrees on 39 of those successfully photographed. Depth-sounder records give indication that another four containers, among

the 41 for which photographic data were not obtained, underwent structural change.

Although one objective of the test program included determination of the behavior of the container contents in the event that external pressures caused by immersion should cause the container to lose its structural integrity, this proved possible in only one instance. A 55-gal steel drum which contained dry solid waste failed by casing rupture that resulted from an implosion. After damage, which occurred at a depth of approximately 1100 ft, particles of concrete, and perhaps other material, were seen emitting from the area until the container was deposited on the bottom. There is evidence to support a conclusion that even normally buoyant materials when subjected to pressures at great depth will not float to the surface but will remain submerged. Tests conducted at sea on several wood blocks tend to verify this phenomenon.

The AEC has indicated that, for the present, the results of this sea-disposal container test would not affect waste-disposal procedures.[49] The Southwest Research Institute, San Antonio, Tex., is correlating and analyzing the results of these sea tests and the data from their laboratory studies on the effects of high pressure on different packaging methods under controlled laboratory conditions.[44,48] This information will provide a basis for recommendations for the design and construction of containers to be used in the disposal of low-level radioactive waste at sea.

Ground Disposal

Kaufman at the University of California has compiled and edited the proceedings[50] of an unclassified conference on ground disposal[41] of radioactive waste. This meeting, sponsored by the AEC's Division of Reactor Development, was held at Berkeley, Calif., in 1959.

The purpose of the meeting was to review the progress made in research and development studies related to ground disposal of low- and intermediate-activity wastes over the past few years, both in the United States and abroad. Major subjects of discussion included (1) operating practices, experiences, and problems at Hanford, Oak Ridge, National Reactor Testing Station, Savannah River, Chalk River (Canada), Saclay (France), and Mol (Belgium); (2) research on ion exchange and adsorption in natural media; and (3) current investigations of hydrodynamic problems in flow through porous media.

Separation of Specific Isotopes

ORNL is continuing its laboratory-scale study of a head-end double precipitation step prior to using ion exchange for the recovery of strontium from Purex type wastes.[51,52] The presence of 1 M sulfate ion in these waste solutions interferes with the recovery of strontium.[53] More than 85 per cent of the sulfate ion was precipitated when excess ferric ion was added to a simulated Purex waste solution and the mixture diluted (with 90 per cent nitric acid) to 50 to 55 per cent nitric acid content. Radiochemical analyses of the experiments indicated that more than 90 per cent of the strontium and more than 50 per cent of the rare earths remained in solution. Evaporating the supernatant solution to the point of nitrate decomposition (130°C), diluting with fuming nitric acid to 63 per cent nitric acid, and heating the solution to 65 to 70°C yielded a precipitate that contained 85 per cent of the original strontium with less than 10 per cent of the original iron and about 30 per cent of the aluminum. A feed solution for further purification by ion exchange was obtained by dissolving the precipitate in dilute nitric acid (6 M).

Laggis and Schmitt at Oak Ridge have investigated ion exchange for the recovery of trace quantities of Np^{237} which occur in certain plant solutions containing fission products, metallic impurities, and enriched uranium.[54] Adsorption and concentration of Np^{237} were accomplished by cation exchange with subsequent purification by anion exchange for removal of fission products. Dowex 50W-X8, a cation resin, adsorbed 99 per cent of the Np^{237} contained in the low-acidity uranyl nitrate solutions (approximately 1 μg of Np^{237} per milliliter). Uranium adsorption on the cation resin appears to be at a maximum of 64 to 67 g of uranium per liter of resin. The uranium is eluted completely from the cation column with 5 to 10 column volumes of 1 M nitric acid, and the neptunium is eluted more than 99.5 per cent with 10 column volumes of 6 M nitric acid. Neptunium-237 leakage to the column effluent and to the uranium eluate was less than 1 per cent when the influent and eluant were

properly maintained at 0.01*M* ferrous sulfamate. Neptunium-237 adsorbs and remains on the resin in the reduced quadrivalent oxidation state but will readily elute at higher valence states. A two-column anion resin system that used Dowex 1-X10 to purify the cation eluate was capable of decontaminating fission products by a factor of 1.4×10^4.

Hanford is continuing its program on the recovery and purification of fission products from various Purex-plant wastes. Flow sheets are being developed which employ precipitation, ion-exchange, and solvent-extraction processes.[55–58] The multicurie Sr^{90} recovery program in the Hot Semiworks was concluded in October 1961. Preliminary material balances indicate a recovery of more than 800,000 curies of Sr^{90}. Over 700,000 curies met product-purity specifications; the remaining material was above specification in cerium.

In addition to the recovery and purification of strontium, the last run in the series of this program was also designed to demonstrate the technical feasibility of a solvent-extraction process for the recovery of cerium and promethium (rare-earth cut).[56–58] A multiple-cycle flow sheet was used. In the first cycle the desired fission products were separated from the inerts in the feed and then partitioned into strontium-rich and rare-earth-rich product streams. Strontium, cerium, and rare earths were extracted into 0.47*M* D2EHPA (di-2-ethylhexyl phosphoric acid)–0.2 *M* TBP solvent from a citric acid-buffered and -complexed system that contained only enough EDTA (ethylene diamine tetraacetic acid) to complex iron. The strontium was stripped into a citric acid solution for a feed to a second-cycle solvent extraction, and the rare earths in the solvent were batch stripped into dilute nitric acid.

In the second cycle the strontium was further purified. The cerium in the strontium-rich stream was complexed with DTPA (diethylene triamine pentaacetic acid). The strontium was then extracted and was subsequently stripped with dilute nitric acid.

In the third cycle the cerium was separated from the promethium-rich rare-earth fraction. The rare-earth by-product from the first cycle was oxidized with permanganate, and the Ce(IV) was batch extracted into D2EHPA solvent. The excess permanganate was reduced to manganous ion with citric acid, and the phases were immediately separated. The solvent phase was then batch contacted with a dilute hydrogen peroxide–nitric acid mixture to reduce the strip of the cerium.

The promethium–rare earth fraction remaining from the cerium-oxidation step contained about 100,000 curies of Sr^{90}. The promethium was sacrificed to permit strontium recovery in a fourth cycle. Two additional cycles of strontium extraction were eventually required for recovery of strontium from solvent wastes and to attain adequate product purity.

Burns and associates at Hanford have summarized for presentation at an AIChE symposium the flow sheets and technology successfully employed in this Sr^{90} program.[57] The work described in this paper has also been extensively reported in previous Reviews.[3]

The recovery of Tc^{99} from Hanford alkaline Purex-waste-tank supernatant was successfully demonstrated on a large scale in shielded ion-exchange equipment.[3,56,57] A 2-in.-diameter ion-exchange column was filled to a depth of 8 ft with Amberlite IRA-401 anion resin, and the supernatant was pumped through the column at the as-received *p*H of 9.9 without addition of reagents or any pretreatment other than removal of solids by centrifugation. Over 110 column volumes of feed were pumped through the column without appreciable breakthrough. Following loading, the column was washed with 2 column volumes of water and 6 column volumes of 0.25*M* nitric acid (to improve fission-product decontamination) and then eluted with 8*M* nitric acid. The absorbed technetium, which amounted to about 5 g, was recovered in only 12 liters (2.5 column volumes) at an average concentration of 0.42 g of technetium per liter. Decontamination factors from cerium, cesium, and zirconium-niobium were 190, 21,000, and 280, respectively. A second column, filled with the cation-exchange resin Duolite C-3, was used for the recovery of cesium.[57] The capacity of this column for cesium was low. Although very nearly complete removal of cesium was obtained from the first few column volumes, 50 per cent breakthrough was reached after passing only 18 column volumes of feed (equivalent to 12 volumes of waste-tank supernatant prior to jet dilution). Following loading, the column was washed with dilute acid and water. This treatment removed 84 per cent of the sodium and 4 per cent of the cesium from the

column. Ninety per cent of the cesium was then eluted in 13 column volumes of 1*M* nitric acid.

Canisters are being developed at Hanford for the off-site shipment of fission products.[53, 56, 58] The fission-product solutions would be evaporated and calcined within these shipping containers. The fabrication of developmental canisters was completed.[53] The fission-product capacities of a $4\frac{1}{2}$-in.-OD by 24-in.-high canister were calculated to be 30, 26, and 55 kilocuries of Sr^{90}, Ce^{144}, and Pm^{147}, respectively.[53] These loadings were based on a maximum decay heat generation of 200 watts and a maximum surface temperature of 325°F in air at 100°F. In the case of Pm^{147}, dilution with other trivalent rare earths results in physical filling of the canister prior to reaching the heat dissipation limit of 200 watts (i.e., a 55-kilocurie Pm^{147} canister will dissipate approximately 90 watts).

Additional laboratory data have been obtained at Hanford on cask shipments of Sr^{90} in the dry condition (i.e., with the interstitial liquid siphoned out in order to afford more free volume to accommodate radiolytic gas production).[9, 55] In these shipments the strontium is loaded on Decalso, an inorganic ion-exchange medium. The final strontium shipment is made in the dry condition.[55] Similar dry shipment has been proposed for a second Decalso strontium cask and for an improved Decalso cesium cask.

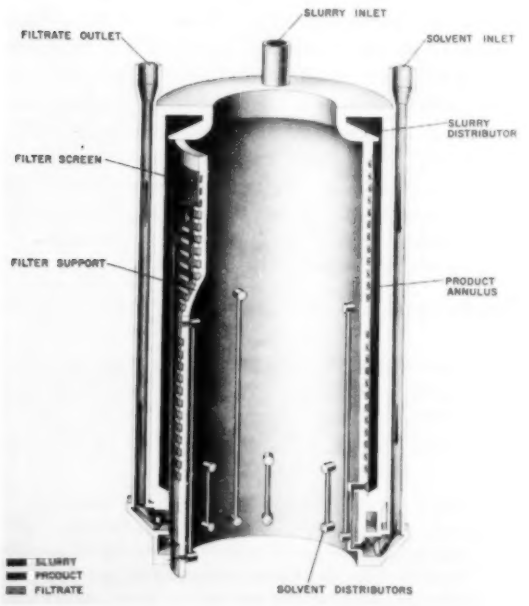

Fig. IV-6 Sr^{90} carbonate filter container for Hanford isotope cask (HAPO II).[57]

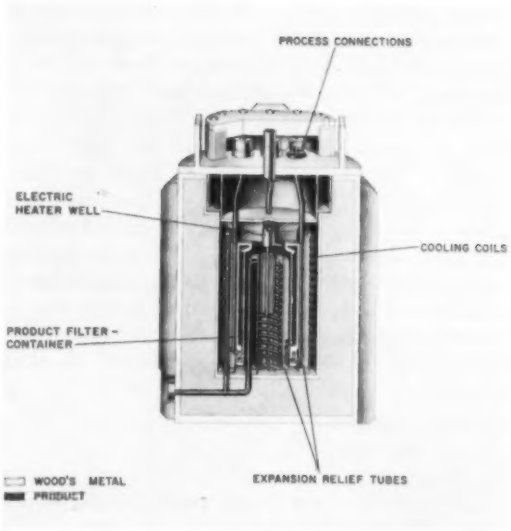

Fig. IV-7 Hanford shielded cask (HAPO II) for shipment of Sr^{90} carbonate filter container.[57]

The effect of heating loaded Decalso on the subsequent elution of strontium and cesium was determined. With both cesium and strontium, temperatures higher than about 100°C resulted in seriously decreased recoveries. The fraction eluted decreased from about 98 per cent for 100°C to about 55 per cent for 200°C and to less than 20 per cent for 300 to 400°C heat-treatments. The shape of the recovery curve closely paralleled the thermogravimetric weight-loss curve, which showed decomposition beginning at about 110°C and a constant weight above about 400°C.

Purified strontium has also been shipped[57, 58] as a dry strontium carbonate in a special filter cask (Fig. IV-6). In this cask the dry strontium carbonate annular filter cake is geometrically restricted to a maximum thickness of $\frac{5}{8}$ in. in order to limit the internal filter-cake temperature.[57] This container, constructed of type 321 stainless steel, fits inside a shielded shipping cask. At the receiving site the fission products are removed from the container by dissolution.

Figure IV-7 shows the assembled strontium carbonate cask. The cask is an externally finned,

hollow cylinder with lead shielding between a 1-in.-thick outer shell and a ½-in.-thick inner shell. The assembled cask is about 3½ ft in diameter, is about 4½ ft high, and weighs about 18,000 lb. A low-melting alloy (Wood's metal) is used to transfer the heat from the filter container to the inner wall of the cask. Solvent-extraction-purified strontium in this cask was shipped in approximately 120,000-curie lots.

Figure IV-8 shows the installation of the shipping cask within a protective buffer designed to withstand the shock, insulation, and fire conditions established as maximum credible incidents. The buffer consists of four coaxial cylindrical steel shells separated by rubber cushions for energy absorption on impact. Air-cooling passages are designed to be sufficient for dissipation of radiolytic heat and, at the same time, to limit flame impingement on the cask proper in case of fire.

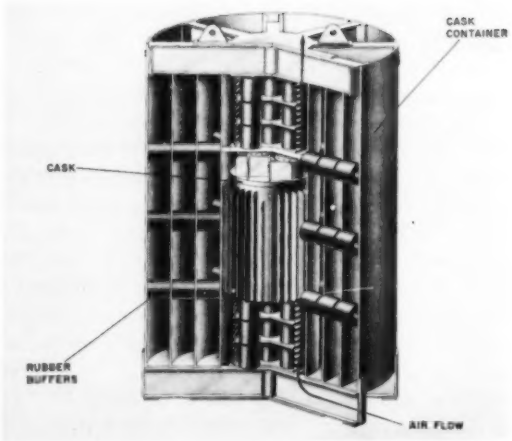

Fig. IV-8 Container for protection of Hanford isotope cask (HAPO II) during shipments.[57]

Since a new cesium-Decalso shipping cask is under consideration at Hanford, a laboratory investigation has been completed to develop a process (to be done in Purex head-end equipment) for increasing the cesium concentration and for decreasing the sodium-to-cesium ratio (relative to neutralized Purex supernatant).[55] The cesium will be precipitated from neutralized Purex supernatant with a slight excess of nickel or zinc ferrocyanide, and the precipitate will be centrifuged, washed, and the cesium dissolved (as cesium carbonate) by heating with a slurry of solid silver carbonate. The dissolved cesium will then be loaded onto Decalso for shipment. Nickel ferrocyanide was found to be somewhat superior to zinc ferrocyanide. The nickel ferrocyanide precipitated approximately 99 per cent of the cesium in the *p*H range 9.7 to 10.4. A two-fold excess of silver carbonate was generally adequate for satisfactory metathesis.

The capacity of Decalso for cesium was also measured as a function of sodium-to-cesium feed ratio.[55] The capacity at a 20,000-to-1 ratio (corresponding to Purex-waste-tank supernatant) was 0.43 g of cesium per liter of Decalso. The capacity (for loading at room temperature) increased to a value of 2.3 g/liter at a ratio of 4500 to 1, 8 g/liter at a ratio of 900 to 1, 23 g/liter at a ratio of 100 to 1, and 90 g/liter at a ratio of 10 to 1. These figures show that heat transfer rather than Decalso capacity will limit the size of individual shipments in the contemplated cask, since the sodium-to-cesium ratio of the product from the carbonate metathesis is expected to be in the range from 10 to 1 to 100 to 1. A decrease of sodium-to-cesium ratio to a value of about 1000 to 1 is all that is required to permit loading 100,000 curies onto 100 gal of Decalso. The sodium-to-cesium ratio can also be reduced to a value of 1000 or less (for subsequent high-capacity loading on Decalso) by absorption on a Duolite C-3 column followed by elution with dilute acid. The capacity of Decalso for cesium was found to be a function of temperature, low temperature favoring absorption and high temperature favoring elution. The capacities at 50 per cent breakthrough of Decalso for cesium (from Purex-waste-tank supernatant) was greater by a factor of 1.7 at 25°C than it was at 60°C.

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Recovery of Uranium from Ores

Chlorination of Uranium Ores

Jangg et al.[1] have made a preliminary study of the chlorination of uranium oxides and concentrates as a means for preparing pure uranium compounds. The results indicated that, although most uranium ores are as readily chlorinated as pure oxides, many impurities which accompany the ore are carried over and condensed with the volatile uranium chloride. Iron, calcium, and magnesium are the chief contaminants of the chloride product. Although uranium chloride can be separated from these compounds either by distillation or by fractional condensation, chlorination of uranium ores appears to be economically feasible only if the ore has relatively high uranium content and if there are no appreciable quantities of other chlorinatable minerals.

Several chlorinating agents were evaluated,[1] but carbon tetrachloride and a mixture of chlorine and methane in a mole ratio of 4 to 1 were the most effective. At a temperature of 500°C, the reaction proceeds rapidly and produces volatile uranium chloride.

Extraction and Purification of Uranium from Ore Concentrates

The most widely used process for producing uranium concentrates is dilute aqueous leaching of the ore with sulfuric acid and, if necessary, an oxidant. The rate and degree of extraction of uranium from its ores by acid leaching depend upon a number of variables: acid concentration, degree of oxidation, leaching temperature, particle size, and the extent to which the uranium minerals are locked or bound by gangue minerals. The dissolution of uranium involves several chemical reactions and is complicated by the presence of numerous impurities in the ore. A published translation gives the results of an investigation on the oxidation and dissolution of uranium oxide in acid media and the effect on these processes of divalent iron compounds.[2] It seems that the oxidation of tetravalent uranium is not determined simply by the normal oxidation-reduction potential. The results show that, where considerable quantities of iron ions were present, incomplete uranium extraction by a mixture of nitric and sulfuric acids was associated with the formation of complexes between Fe^{2+}, SO_4^{2-}, and NO_3^- ions.

Recovery and concentration of uranium from acid sulfate leach solutions may be effected by stationary or moving-bed anion-exchange resins. Simard et al.[3] have studied the possibility of applying directly a solvent-extraction treatment of nitrate eluates from ion-exchange resins. The mechanism of extraction with TBP (tributyl phosphate) is favored by high nitric acid concentrations and depressed by the presence of sulfate ions. A variety of solvents were evaluated[3] on both nitrate and sulfate eluates from exchange resins: TBP, dibutylbutyl phosphonate, and di-2-ethylhexyl phosphonate on nitrate eluates; and tricapryl amine on sulfate eluates. Results of the preliminary investigations indicate that, from an over-all viewpoint, solvent-extraction purification of nitrate eluates with dibutylbutyl phosphonate appears to be preferable.

Lang and Nethaway at Mallinckrodt Chemical Works[4] have investigated the effect of sulfate ions on the extraction of uranium from a nitric acid solution into a 30 per cent TBP–hexane solution. Sulfate definitely inhibits the extraction of uranium from solutions that have a low

uranium concentration. This effect can be partially overcome by increasing the salt nitrate concentration of the aqueous phase. In solutions with a high initial uranium concentration, the presence of soluble sulfate appears to have little effect on the extraction of uranium by TBP.

At the uranium plant operated by Vitro Chemical Company, uranium is leached from the ore body with dilute sulfuric acid that contains sodium chlorate as an oxidant. The uranium is extracted from the liquor with 0.1*M* dodecyl phosphoric acid in kerosene and stripped with 10*N* hydrochloric acid. It was observed that, along with uranium, scandium was extracted into the solvent. Since scandium was not stripped by hydrochloric acid, the element continued to extract selectively into the organic phase at the expense of uranium loading. A description of a process developed at Vitro for recovering scandium from poisoned solvents was recently published.[5] The process is based on stripping the solvent with hydrofluoric acid. Through a sequence of chemical separation operations, a scandium oxide product of 99.5 per cent purity is produced.

Production of Uranium Dioxide

Enriched Uranium Dioxide

A report describing the pilot-plant-sized apparatus built at Chalk River for the production of highly sinterable uranium dioxide powder enriched in U^{235} was recently published by Atomic Energy of Canada Ltd.[6] The process employs the ADU (ammonium diuranate) route for the manufacture of uranium dioxide. The required U^{235} content is obtained by blending, in solution, enriched uranium and natural uranium. The enriched uranium, obtained as uranium dioxide, is dissolved in nitric acid in a geometrically safe vessel. The enriched solution is blended with a uranyl nitrate solution of natural uranium to give a uranium concentration of approximately 150 g/liter. The mixture is continuously pumped into a small tank where ADU is precipitated by adding ammonium hydroxide at a flow rate adjusted to provide a *p*H of 7.2 in the precipitation tank. The ADU that is formed overflows as a slurry, and the slurry is filtered on a continuous belt filter. The cake is dried in air at 120 to 180°C and is crushed before being loaded into 1-in.-deep trays in the reduction furnace. Ammonium diuranate is reduced at 450°C with 10 vol.% hydrogen in nitrogen. A test for completeness of reduction is made by observing the temperature rise of the powder obtained by a sequence of operations using higher concentrations of hydrogen as the reducing gas. The reduction is concluded at a furnace temperature of 600°C. The uranium dioxide product is crushed and sintered in hydrogen for 1 hr at 1650°C. This plant has consistently produced uranium dioxide powder that has sintered to a density of 10.56 g/cm^3.

The plant was designed with emphasis on safety from the criticality viewpoint by basing the principal control on geometric limitations. The parameters set for criticality safety are as follows:

1. The inner diameter of piping, tanks, etc., must not exceed 5 in.
2. Pipes greater than 1 in. in inside diameter must be at least 2 ft apart and at least 2 ft from any wall. Rows of such tanks must be at least 5 ft apart.
3. The thickness of any slab of solution, precipitate, or powder may not exceed 1 in.
4. Furnace insulation must not contain more than the equivalent of a 1-in. thickness of carbon, beryllium, or zirconium. Aluminum oxide is preferred for the inner inch of insulation.
5. Large-diameter (>5 in.) weigh tanks are permitted for use with natural uranium, provided that there is no possibility of backflow from the enriched-uranium section of the process.
6. Not more than 2 kg of U^{235} in enriched uranium may be in the system (including transfer containers, dissolvers, mixers, precipitators, and filters).
7. Each furnace may contain up to 1 kg of U^{235}.
8. The maximum enrichment to be used is 20 wt.% U^{235} in uranium.
9. A total of 500 kg of natural uranium may be stored in the plant area.

Reduction of Uranium Trioxide

The mechanism of the hydrogen reduction of uranium trioxide is not readily elucidated owing to the complexity of the uranium oxide system. At least four thermodynamically stable oxides have been completely characterized, and several additional oxides have been reported. Poly-

morphism, solid solution, and metastability phenomena further complicate the uranium-oxygen system.

The kinetics of the hydrogen reduction of uranium trioxide of both high and low surface area have recently been investigated. DeMarco and Mendel[7] have studied the reduction of high-surface-area amorphous uranium trioxide (26 m^2/g) to uranium dioxide and have suggested that the reaction occurs in two separate steps: the trioxide is completely reduced to $UO_{2.56}$ and then to $UO_{2.0}$. Kinetic investigations indicate that both steps in the reaction are primarily controlled by adsorption of hydrogen on the product oxide surface.

Morrow et al.,[8] in their investigation of the reduction of low-surface-area uranium trioxide (< 1.2 m^2/g), concluded that the observed kinetics were best interpreted in terms of hydrogen chemisorption on the solid surface as the rate-controlling step. An increase in surface area and pore volume occurred during the reaction, and an intermediate compound ($UO_{2.6}$ to $UO_{2.7}$) was formed. The initial rate of reduction was found to be directly proportional to the surface area of the uranium trioxide and to the 0.78 power of the hydrogen partial pressure. The addition of sulfate ions to the trioxide greatly increased the surface area and therefore the reaction rate.

Coating of Uranium Dioxide Particles

The encapsulation of individual uranium dioxide particles with ceramic coatings by fluidized-bed techniques has been demonstrated by workers at Battelle Memorial Institute (BMI). A description of the procedures used in coating particles with alumina by hydrolysis of aluminum chloride vapor appeared in an earlier Review.[9] This technique has been extended recently to include the deposition of beryllium oxide and magnesium oxide.[10–12]

Magnesium oxide was successfully deposited on uranium dioxide by hydrolysis of magnesium iodide in a fluidized bed.[12] Translucent coatings up to 21 μ thick were produced, and they appeared to be dense and void free. However, magnesia coatings on a dense uranium dioxide substrate were found to be cracked when cooled to room temperature. Coatings that were free from cracks were observed on particles that had a porous oxide substrate. Cracking of magnesium oxide is attributed to the large difference in thermal expansion coefficients of uranium dioxide and magnesia.

Beryllia coatings[10,11] had been applied to uranium dioxide particles by hydrolysis of beryllium chloride at 700 and 1100°C by use of the apparatus and techniques developed for alumina coating. Oxide coatings up to 26 μ thick were found to be free of voids and relatively dense as indicated by acid-leach data; however, when the equipment design was modified in an effort to permit the deposition of thicker coatings in a continuous operation, coatings of inconsistent quality were obtained. In an attempt to obtain uniform beryllia coatings, several tests were made by use of the thermal decomposition of beryllium basic acetate in an atmosphere of hydrogen at 500 to 800°C. The product coatings from these tests were glassy smooth, contaminated with carbon and residual water, and soluble in nitric acid. It is suggested that the presence of silicon and other minor impurities in the beryllium chloride-hydrolysis process may have contributed to the high quality of the deposits.

Recent work[12] has been directed toward the use of the direct oxidation of beryllium chloride as a means for producing sound beryllia coatings. Initial trials at 1000°C indicated that the oxidation rate was very low; however, the reaction was found to be catalyzed with steam and carbon dioxide to an extent to make practical the deposition of beryllium oxide by direct oxidation.

Production of Uranium Tetrafluoride

Kinetics of the Hydrofluorination of Uranium Dioxide

Tomlinson et al.[13] have investigated the kinetics of the reaction of uranium dioxide with gaseous hydrogen fluoride in the temperature range 200 to 450°C. The reaction is complicated by the loss of surface area which results from crystallite expansion and sintering of the uranium tetrafluoride. The initial stages of the reaction are very rapid and are accompanied by particle overheating and a decrease in surface area. Uranium tetrafluoride sintering is mainly the sintering of crystallites within a particle rather than agglomeration of particles. After the initial high reaction rate, the rate decreases

and the particle surface area remains constant until the reaction is complete. It was observed that the extent of conversion to uranium tetrafluoride increased as the uranium dioxide surface area was increased from 0.15 to 2.1 m^2/g. Above this value the reaction rate was generally unaffected by surface-area changes.

The reaction rate during the period of constant-particle surface area was directly proportional to the hydrogen fluoride partial pressure and had an activation energy of 9.6 kcal/mole. This comparatively low activation energy suggests that the diffusion of gases through the pores of the particles would appear to be the most likely rate-controlling step.

Studies by Schare[14] at National Lead Company of Ohio on the hydrofluorination reaction have shown that there is a deviation from the expected rate expression during the initial stage of the reaction which is attributed to thermal damage (sintering) of the particles. When thermal damage is severe, complete conversion to uranium tetrafluoride is hindered. These conclusions essentially substantiate the work of Tomlinson et al.[13]

Activation of Uranium Dioxide for Uranium Tetrafluoride Production

The ease of conversion of uranium dioxide to uranium tetrafluoride with hydrogen fluoride depends largely on the reactivity of the oxide. Usually the degree of reactivity of uranium dioxide is controlled by regulating the conditions of the preceding steps of thermal denitration of uranyl nitrate to uranium trioxide and reduction of the higher oxide.

Low-reactivity uranium dioxide can be made more reactive by successive oxidation to U_3O_8 and reduction to uranium dioxide. Bard et al.[15] at Los Alamos have studied the mechanism of activation of uranium dioxide by successive oxidation and reduction. Surface-area, pore-size, and X-ray measurements indicated that activation of aggregates of microcrystalline uranium dioxide resulted from separation, but not reduction in size, of primary crystallites. Repeated successive oxidation and reduction of the uranium dioxide produced first an increase in surface area (at constant crystallite size) because of separation of adhering microcrystals, and then a decrease in bulk density (with both crystallite size and surface area constant) due to further separation of the detached microcrystals. These physical changes resulted in greatly increased chemical reactivity toward hydrogen fluoride gas and oxygen. The hydrofluorination of uranium dioxide to uranium tetrafluoride was found to be sensitive to changes in porosity of the uranium dioxide during the reaction. It was observed that the reactivity of activated uranium dioxide to hydrogen fluoride was greatly affected by the conditions of the oxidation step.

The activation of uranium trioxide produced from the continuous pot denitrator[16] by a reduction-oxidation-reduction cycle has also been studied at National Lead Company of Ohio[17] in plant-scale tests using fluidized-bed reactors. The conditions for the tests were set to simulate a plant-scale process that would incorporate two-stage cocurrent fluid beds for both the reduction and oxidation steps of the process and a normal production reactor bank for the second reduction and hydrofluorination. In a normal reduction-hydrofluorination reactor bank, a two-stage cocurrent fluid bed followed by a screw reactor is used for the reduction reaction. Hydrofluorination takes place in three screw reactors arranged in series.

Ground, continuous pot denitrated uranium trioxide was reduced with dissociated ammonia in the fluid-bed reactors at 595°C. The product (uranium dioxide) was oxidized to U_3O_8 with 50 per cent excess air. Changing the oxidation temperature over a range of 370 to 480°C appeared to have no effect on the subsequent processing steps. The U_3O_8 produced in the intermediate oxidation step had a lower bulk density than the parent uranium trioxide and uranium dioxide. Rereduction was conducted at 550°C in 100 per cent excess dissociated ammonia. The activated uranium dioxide was hydrofluorinated in the bank of three screw reactors in 20 per cent excess hydrogen fluoride under preset temperature conditions that ranged from approximately 246°C at the solid-feed inlet to 550°C at the product outlet. The resulting uranium tetrafluoride was about 10 per cent lower in density than normally produced uranium tetrafluoride. High-assay green salt was produced in the three screw reactors at a production rate approximately 30 per cent greater than that achieved without activation. Analysis of samples from the second of the three hydrofluorination screw reactors averaged 97.6 per cent uranium tetrafluoride, which indicated that metal-grade material could be produced in two screw reactors rather than in three as at present.

A plant-scale investigation has been conducted at National Lead Company of Ohio to evaluate the effects of ammoniation of uranyl nitrate liquor upon subsequent conversion of uranium trioxide to uranium tetrafluoride at various feed rates.[18] It had been observed previously that ammoniation resulted in increased chemical reactivity of the uranium trioxide powder. Data were accumulated on feed material that contained 6000 to 33,000 ppm ammonia (uranium basis) and 1250 to 1500 ppm sulfate. An analysis of the uranium tetrafluoride product in terms of percentages AOI (ammonium oxalate insolubles) and uranium tetrafluoride indicated that variations in the ammonia content of uranyl nitrate over the range studied had no significant effect on the quality of the green salt produced. The failure to show any benefit from increased ammoniation may be obscured by the accompanying sulfation of the feed. The apparent disagreement between these conclusions and previous results may be reconciled by the fact that previous work was performed on nonsulfated material and that this study was concerned with the effects of increase in ammoniation level rather than with the presence or total absence of ammonia. The study also showed that the rate at which uranium trioxide was fed to the reduction hydrofluorination reactor bank had a significant effect on the percentages of uranium tetrafluoride and AOI in the product.

Preparation of Uranium Carbides

In the preparation of uranium monocarbide by the reaction between uranium metal and alkane hydrocarbons, propane has shown greater reactivity than methane. Sano et al.[19] have suggested that this increase in reactivity is caused by the production of free radicals during the reaction. Workers at United Nuclear Corporation[20] have established reaction conditions for the production of uranium monocarbide that contains 4.4 ± 0.1 wt.% carbon and 4.8 ± 0.1 wt.% carbon by reaction of hydrided metal with propane. The optimum conditions for the production of the 4.4 ± 0.1 wt.% carbon species were to carburize at 600°C for 30 min. The conditions required to produce the higher carbon-content material were to carburize for 40 min at 625°C. Uranium carbide powder that contained 4.3 wt.% carbon was vacuum sintered for 3 hr to obtain a density of 13.8 g/cm^3. A density of 12.0 g/cm^3 was obtained with 4.7 wt.% carbon powder by vacuum sintering 3 hr at 1800°C. Sintering of the high-carbon material was complicated by its brittle nature, poor compressibility, and uranium evaporation during sintering.

Uranium dicarbide may be produced[21] by the reaction between powdered uranium metal and propane at temperatures above 800°C. The reaction appeared to occur in two stages. During the first stage both uranium monocarbide and uranium dicarbide were synthesized by the reaction between uranium and free radicals produced by the pyrolysis of propane; in the second stage of the reaction, uranium monocarbide slowly reacted with secondary products of propane and synthesized the dicarbide.

Workers at Argonne National Laboratory (ANL)[22] have investigated the direct reaction of uranium dioxide and elemental carbon as a means for producing uranium monocarbide. The attractive features of this preparatory method are (1) the ease of scaleup for large production rates, (2) the availability of reactants, and (3) the fact that the process would involve conventional powder techniques. High-quality uranium carbide has been produced by reacting stoichiometric quantities of uranium dioxide and carbon in a vacuum at 1650°C for 48 hr. The resulting clinker was found suitable for processing into sintered pellets. Owing to production of gas during the reaction, control of the firing conditions was difficult. Therefore efforts were directed toward conducting the reaction in a flowing gas system. Preliminary results indicated that the kinetics of the reaction between uranium dioxide and carbon required large surface contact area between the reactants if complete reaction was to be achieved at moderate temperatures in a reasonable time. A successful method of obtaining suitable carbon distribution was to add the carbon as a soluble carbonaceous material (petroleum pitch in alcohol) to the mixing operation so that, after drying, each of the uranium dioxide particles was coated with the carbonaceous material. The blended material was compacted into pellets and prefired at 900°C to carburize the pitch. Uranium monocarbide was produced by firing in a flowing argon gas stream for 1 hr at 1450°C, followed by a second firing for 1 hr at 1700°C in an evacuated (10^{-4} mm Hg) system. No uranium dioxide was

detected by X-ray diffraction in products that were prepared by this method.

The possibility of synthesizing uranium monocarbide in liquid-metal media is currently being explored at ANL.[23,24] Uranium monocarbide has been prepared by precipitating with carbon the uranium dissolved in a volatile liquid-metal solvent. Successful preparations have been made[24] using a 10 wt.% magnesium–zinc solvent, a carbon excess of 50 per cent, and a temperature of 850°C. In this system the uranium monocarbide that is formed settles rapidly, and any unreacted carbon rises to the surface. The segregation of these ingredients in the solidified ingot is sufficiently sharp to permit the removal of unreacted carbon by cropping the ingot prior to retorting.

Initial success of this preparatory technique has prompted investigation of the preparation of other uranium and plutonium compounds.[24] Two uranium silicides have been prepared: (1) USi_3 from a cadmium solution of uranium at 700°C and (2) U_3Si_2 by reacting stoichiometric quantities of the two elements in an 8 wt.% magnesium–zinc solution. Work has also been initiated on the preparation of plutonium carbide. Preliminary tests[24] have produced only the sesquicarbide, Pu_2C_3.

A review of methods currently being studied for preparing uranium monocarbide in bulk and powder form has recently been published.[25] Included are details on the uranium-carbon reaction, uranium dioxide–graphite reaction, and uranium-alkane reactions.

Production of Uranium Metal

Electrolytic Reduction of Uranium Dioxide

High-quality uranium metal can be made from uranium dioxide by fused-salt electrolysis using a consumable anode that contains a uranium dioxide–carbon mixture. The reduction cell consists of a cylindrical graphite crucible that serves both as the cathode of the cell and as a container for the molten electrolyte and molten metal. Details of the three types of anode configurations that are currently being evaluated at Mallinckrodt Chemical Works were given in a previous Review.[26] The most satisfactory anode arrangement appears to be a configuration that provides an electrically neutral basket to contain the uranium dioxide–carbon pellets.[27] The anode is a perforated graphite container that holds chunks of the uranium dioxide–carbon mixture. The cell current is supplied via graphite rods that extend into the bed of pellets contained in the basket. This arrangement has virtually eliminated formation of carbon tetrafluoride at the surface of the graphite basket.

It has been observed[27] that operation of the electrolytic cells for extended periods generally leads to the formation of a layer of black material at the electrolyte surface. This layer has an electrical conductivity that is sufficiently high to lead eventually to short-circuiting of the cell. Analyses of this material show the major ingredient to be electrolyte, although it appears that carbon or graphite particles are essential ingredients for the layer formation. Introduction of carbon dioxide over the surface of the electrolyte is quite effective in preventing the formation of a conducting layer. The action of the carbon dioxide is probably that of burning the carbon particles.

An alternative method for control of the conducting layer would be to operate the electrolytic cell with a frozen crust of electrolyte. This would require the use of an electrolyte with a liquidus temperature of 1150°C and the establishment of a temperature gradient in the cell such that the upper walls are below the liquidus temperature. Operation with a frozen crust has been attained for brief periods, but stable operation could not be maintained.

Reduction of Uranium Tetrafluoride

High-quality green salt is produced at National Lead Company of Ohio from various enriched-uranium residues by an aqueous precipitation process (Winlo process)[28] to yield a hydrated uranium tetrafluoride. Winlo green salt contains ¾ mole of water of hydration, and this adversely affects its reduction to metal. Heating to over 370°C is required to remove the water of hydration. Previous work[28] had shown that hydrated Winlo green salt could be satisfactorily reduced to metal by blending it with green salt produced from the reduction of uranium hexafluoride. A series of pilot-plant-scale tests were recently conducted to determine the reduction characteristics of various forms of dehydrated Winlo uranium tetrafluoride.[29]

High derby yields and good separation of metal and slag were obtained from reductions

of dehydrated Winlo green salt that was made in reactors lined with magnesium fluoride slag. The moisture content of the dehydrated uranium tetrafluoride was approximately 0.05 per cent. Average derby yield was 98 per cent, and none of the derbies was misshapen. Increasing the uranyl fluoride content of the dehydrated green salt to 2.3 per cent did not affect the derby yield or quality but greatly increased the firing time. The firing time was also increased by blending 16 per cent hydrated Winlo green salt with dehydrated material.

The tap density of dehydrated Winlo green salt was 3.2 g/cm^3, which is low in comparison with 3.7 g/cm^3 for uranium dioxide-source green salt. Ball-milling the dehydrated salt increased the tap density to 3.6 g/cm^3; thus an increase of 7 per cent in the tetrafluoride charge was made possible. However, the milled charge gave no better derby yields or slag separation than the unmilled material.

Very good derby yields (97.5 per cent) were obtained from reductions of 16 per cent dehydrated green salt that was blended with 84 per cent uranium tetrafluoride produced from the reduction of uranium hexafluoride. The appearance of the derbies, however, was typical of those obtained from the reduction of 100 per cent uranium hexafluoride-source material (irregular, rough, and gas-pocked). The average derby yield of the hexafluoride-source material was only 94.3 per cent.

The magnesium presently used in most uranium plants as a reductant for uranium tetrafluoride is obtained by chipping magnesium ingots cast from magnesium that was produced by the Pidgeon process. This process consists of the reduction of dolomite under vacuum by ferro-silicon at 1150°C and by distillation of the product. The crystalline rings of magnesium obtained are termed "crowns." These crowns consist of rather loosely bound, large crystals that are relatively easy to separate by crushing. Crushed crown magnesium differs from chipped magnesium primarily in its higher specific surface area, hydrogen content, and nitrogen content. If the crushed crown material can be used for uranium production, a large part of remelting, casting, and chipping costs incurred in magnesium production can be bypassed. The savings have been estimated at $0.06/lb of magnesium.

Crushed crown magnesium has been evaluated at Mallinckrodt Chemical Works on a small scale (4-kg dingots of uranium metal) for possible use in uranium production.[30] The results of these tests indicated that the purity and hydrogen content of the uranium products were acceptable when using −10 +30 mesh crushed crown magnesium. In comparison with chipped magnesium, crude uranium yields were slightly lower (3 per cent) when crushed crown magnesium was used. No critical problems in either handling or bomb behavior were noted. It is suggested that the yield losses might be overcome in plant-scale operation.

Reduction of Uranium Trichloride in Fused Salts

Studies on a fused-salt process for the preparation of uranium metal have been made by French workers at CEN[31] as a purification technique. Very pure uranium metal can be obtained by electrorefining in a fused salt that contains 30 wt.% uranium trichloride dissolved in a lithium chloride–potassium chloride eutectic.[31] Impure uranium was used as the anode, and molybdenum was used as the cathode. The electrolysis was conducted at 400 to 450°C under an inert atmosphere of argon. It was observed in laboratory tests that the presence of moisture introduced many operational problems: the impurity level in the product uranium increased; the cathode current efficiency decreased from 80 to 10 per cent; and the anode was substantially corroded, with the apparent anode current efficiency rising from 90 to about 120 per cent.

Partridge et al. at Harwell[32] have recently developed a method for preparing solutions of uranium trichloride in lithium chloride–potassium chloride eutectic. The process involves the reduction of a heavy-metal chloride by uranium in the lithium chloride–potassium chloride eutectic. Preparation experiments on a 1.5-kg scale were undertaken to produce uranium trichloride concentration in the eutectic of 30 wt.%. The reduction reaction was carried out at 500°C by immersing a uranium rod in a solution of cadmium chloride in the lithium chloride–potassium chloride eutectic. After 4 hr of reaction time, the residual quantity of cadmium chloride (0.3 wt.%) was removed by electrolysis at 0.6 volt under vacuum. Cadmium metal was removed from the salt by decanting the molten

salt. The final cadmium chloride in the salt was 0.007 wt.%.

Recovery of Uranium from Uranium Tetrafluoride Scrap

The reversion of impure uranium tetrafluoride to a suitable refinery feed was studied at Mallinckrodt Chemical Works.[33] This material contains iron and nickel impurities of such high concentration that blending with production material is not feasible. The wet reversion of uranium tetrafluoride to hydrated uranium dioxide is accomplished by adding the impure uranium tetrafluoride to a boiling solution of 23 per cent sodium hydroxide. The reaction proceeds according to the equation $UF_4 + 4NaOH \rightarrow UO_2 \cdot 2H_2O + 4NaF$. Fluoride that is contained in the slurry is removed by diluting with water, followed by settling and decantation. A flocculating agent is added to increase the settling rate of the uranium oxide. Any residual fluoride is complexed by adding hydrated alumina to the thickened slurry. The uranium oxide slurry is dissolved in 45 per cent nitric acid at 82°C, and the final uranyl nitrate solution is recycled to the refinery operation. The recycled uranyl nitrate solution has been found to be entirely suitable as a feed material.

Laboratory tests at National Lead Company of Ohio have shown that thermite bomb residues composed of uranium tetrafluoride, magnesium fluoride, and magnesium metal can be recovered by a reversion process that employs a potassium hydroxide solution.[34] Essentially complete reversion to oxide was attained by digesting the scrap residues in 40 wt.% potassium hydroxide solution for 2 hr at 80 to 90°C. The reverted cake was digested with nitric acid at 60°C, and approximately 99.9 per cent of the uranium values was recovered. After digestion, the feed slurry was successfully processed in a ½-in.-diameter pulse column that used TBP diluted with kerosene as the uranium extractant. An addition of 20 g of aluminum per liter for fluoride complexing was essential to guarantee a uranium concentration in the raffinate of less than 0.2 g/liter.

Thorium

Chlorination of Monazite

The usual method for separating thorium from monazite involves chemically decomposing the ore and fractionally precipitating either the valuable elements (thorium and rare earths) or the gangue. Monazite is essentially an orthophosphate of the rare-earth elements of low atomic weight and contains from 4 to 10 per cent thorium and up to 0.5 per cent uranium, depending on the source of the ore. Both caustic-soda and sulfuric acid digestion processes have been used commercially as the initial step in the recovery of the valuable elements.

Hilal et al.[35] have recently conducted laboratory-scale tests on the recovery of thorium from monazite by chlorination with chlorine in the presence of charcoal at 900°C. Process conditions were established in an apparatus constructed of silica tubing and consisting of a chlorinator and two condenser chambers. Approximately 98 per cent of the thorium content of the monazite was recovered as thorium tetrachloride in a condenser maintained within a temperature range of 550 to 475°C. The thorium tetrachloride condensate averaged 99 per cent purity, with phosphate and iron being the major contaminants. The rare earths, whose chlorides are not volatile, remained in the chlorinating vessel. Uranium was collected in the second condenser maintained at 475 to 180°C.

Preparation of Spherical Thorium Oxide Particles

The possible use of spherical thorium oxide particles as a homogeneous reactor blanket material or, together with uranium oxide, as a reactor fuel, has prompted investigations into methods for preparing individual thorium oxide particles 5 to 60 μ in diameter. Workers at ORNL[36,37] have developed a process for preparing thorium oxide–uranium oxide particles based on the fact that drying and calcination of a thoria hydrosol produces large, near-theoretical-density particles of thorium oxide. The process consists of four steps: (1) preparation of thorium oxide from thorium nitrate, (2) dispersion of the oxide to a hydrosol, (3) drying of the sol to produce a gel, and (4) calcination of the gel to the oxide.

Thorium nitrate is hydrolyzed in steam at 390°C and 1 atm pressure to give a thoria powder with a nitrogen-to-thorium mole ratio of 0.15. The powder is dispersed in water to form a stable sol 2*M* in thorium. The sol is aged 14 hr under reflux boiling, and uranium is added as ammonium diuranate, hydrated uranium tri-

oxide, or uranyl nitrate. The sol is evaporated to dryness at 70°C, and gel fragments are yielded. These fragments are then precalcined by slowly treating under a prescribed schedule to 500°C. Final calcination is conducted in hydrogen at 1200°C for 4 hr. Thoria-urania particles (containing 4.4 wt.% uranium) that were prepared by this process had a particle density of 9.9 as compared to a theoretical density of 10.0.

Thorium oxide–uranium oxide spheres also have been produced at ANL on a pilot-plant scale.[38] Thorium nitrate was dissolved in water to form a nearly saturated solution (2.7*M*). Anhydrous ammonia gas was added until the entire solution gelled. After the gel formed, additional thorium nitrate solution was added to produce a stable sol. Uranyl nitrate hexahydrate was added to the sol, and the mixture was blended by vigorous agitation. Gelling was completed by spraying the feed solution into an atmosphere of ammonia. The resulting gelled particles were washed with ammonium hydroxide solution, air dried, and finally washed with methanol. The average diameter of fired spheres ranged between 14 and 23 μ, whereas the spheres before firing averaged 60 μ in diameter. Optical observations of the fired spheres showed that most of the particles retained their spherical shape.

Spherical thorium oxide particles have also been prepared by spraying a thorium sol into certain organic solvents to produce spheres of thorium hydroxide which may be fired to produce oxide spheres of 50 to 60 μ in diameter.[39] Of various organic solvents tried, isopropyl alcohol proved to be most effective. A sol concentration greater than 1.5*M* was found necessary to ensure a consistently satisfactory product.

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